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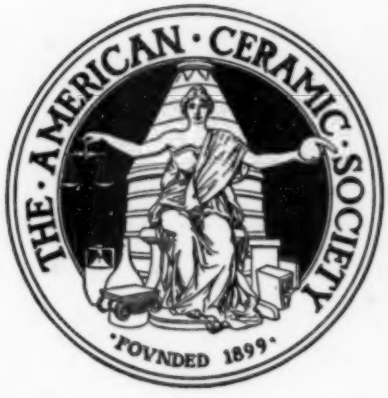

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THE JOURNAL
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THE AMERICAN CERAMIC SOCIETY

Volume 27 October 1, 1944 Number 10

VOLUME CHANGE ATTENDING LOW-TO-HIGH INVERSION OF CRISTOBALITE*

By M. D. Beals† and Samuel Zerfoss‡

Abstract

The volume expansion of cristobalite, as it passes through the low-temperature inversion range, was studied by means of a dilatometer in which the cristobalite expanded against a column of mercury. The volume change was measured in a capillary tube attached to the mercury column. The temperature of inversion is a function of the previous history of the cristobalite sample. A volume change of 7% was obtained upon inversion. The volume change was found to depend on the previous heat-treatment of the sample, the presence of added catalysts, and the source and grain size of silica. All of these factors affect the amount of cristobalite present and hence the change of volume on inversion of the cristobalite. Several samples of cristobalite from used silica brick were studied. The information is applied to the problems of silica refractories.

I. Introduction

The mineral analysis of silica brick might provide much valuable information about the heat-treatment of silica in commercial practice. None of the various methods available for mineral analysis, such as the use of heavy liquids and micrometric analysis of thin sections, is satisfactory because of the intimate intergrowth of the three mineral phases, quartz, cristobalite, and tridymite, which are commonly present in the silica-brick samples.

It was thought that an estimation method could be based on the volume expansion of cristobalite during its high-to-low inversion, assuming, of course, that the volume change during inversion within a series of samples was reproducible. Thus, if the magnitude of this change for pure cristobalite were known, the amount of cristobalite in a mixture could be estimated.

An apparatus for the determination of volume expansion was developed, and the usual procedure of calibration was carried out. It was learned that the assumption of reproducibility of volume expansion of cristobalite, implicit in such a proposed method, was questionable. Although the present work provides no entirely satisfactory method for the estimation of the cristobalite content, the results are interesting in that they provide information about the characteristics of this mineral. Some of the known properties of the two forms of cristobalite are summarized, and the characteristics of the inversion are illustrated by means of data obtained with the volume expansion apparatus.

The inversions of silica are of two kinds, (1) the sluggish type, such as quartz to tridymite, and (2) the "prompt-reversible," "high-low" or "alpha-to-beta" variety. To the latter kind belong the rapid reversible inversions which occur within a lattice type.

There are three fundamental lattice types for the compound silica, corresponding to the three minerals, quartz, cristobalite, and tridymite. The ultimate unit of structure is the silicon-oxygen tetrahedron, in which each of the oxygens is shared between two silicon atoms so that the tetrahedral groups have common corners. By linking these tetrahedral groups according to three different schemes, the three lattice types can be vizualized.

During the sluggish inversion between lattice types, as between quartz and tridymite, the links between tetrahedra probably must be broken and then rejoined to form the new lattice. The large amount of work involved in such a rearrangement accounts for the sluggishness of the inversion. In the case of the high-low inversions, the links between tetrahedra are preserved but the tetrahedra probably undergo a rotation and displacement.[1] Less energy is required to effect these displacements, which results in the rapidity and easy reversibility of these high-low inversions.

High cristobalite has a cubic structure in which the

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[1] W. L. Bragg, Atomic Structure of Minerals, pp. 33–90. Cornell Univ. Press., Ithaca, N. Y., 1937. 292 pp.; *Ceram. Abs.*, **17** [6] 231 (1938).

unit cube contains eight molecules of silica. The length of the unit cube is reported by Barth[2] as 7.16 a.u. at 500°C. and by Ewald and Hermann[3] as 7.12 a.u. at 290°C.

Low cristobalite is either orthorhombic or tetragonal with a unit (pseudocubic) cell length of 7.00 a.u. and a calculated density[3] of 2.30 ± 0.03. Ewald and Hermann[4] give $a = 6.94$ a.u. Assuming that low cristobalite is tetragonal, the values of the cell dimensions[5] for a pseudocubic cell are $a' = 7.02 \pm 0.005$ a.u. and $c' = 6.92 \pm 0.005$ a.u.

The inversion of the alpha or high cristobalite to the beta or low form has the following characteristics: (1) The inversion is rapid and completely reversible. (2) The volume change on inversion ranges from 2 to 5%, according to Rieke and Endell.[6] Cohn[7] has determined that the heat of inversion is 6 cal. per gm. (3) The temperature of inversion depends on the previous thermal history of the sample.[8] (4) The inversion is subject to hysteresis[9]; this latter point is well illustrated by the present data. (5) The temperature of the inversion and quite probably the volume change depend on the source of silica used.[10] (6) The inversion is possibly influenced by the presence of small amounts of impurities (mineralizers) in the sample.[10]

The influence of thermal history of the sample was first noted by Fenner.[11] The higher the inversion temperature the higher is the temperature at which the cristobalite is formed or brought to equilibrium. The cristobalite in the hot end of a silica brick in use in the open-hearth furnace[9] thus has an inversion temperature of 270°C., whereas cristobalite formed from glass by devitrification[12] at 900°C. has an inversion temperature of 201°C. The inversion appears to take place over a small range of temperatures, and the temperature obtained on heating is higher than that obtained on cooling.

Weil[13] examined five different samples of natural cristobalite and gave inversion temperatures ranging from 175° to 250°C. as determined on the hot stage of a polarizing microscope.

Pierce and Austin[8] measured the temperature of inversion of cristobalite in samples cut from the used silica brick taken from the roof of a basic open-hearth furnace. Samples were taken at progressive distances from the hot face; and because there is a temperature gradient from the hot face toward the cold end of the brick, they assumed that the samples contained cristobalite which had been brought to equilibrium at temperatures corresponding to the gradient. They found that the temperature of inversion decreased as the distance of the sample from the hot face increased (that is, as the temperature of equilibrium decreased).

Kondo and Yamauchi[14] state that the transition of cristobalite (made from quartz by mineralization) takes place at about 250° ± 10° C. on heating and 230° ± 10°C. on cooling.

Van Nieuwenburg and Zijlstra[15] give the inversion temperature of cristobalite, formed in the devitrification of a high-silica borosilicate glass in the temperature range 625° to 950°C. as 201° to 218°C. on heating and 192° to 240°C. on cooling. They also suggest that the inversion temperature and the temperature hysteresis change as the crystals grow or proceed through some sluggish transformation which is induced by continued heat-treatment.

Taylor and Lin[10] give inversion temperatures ranging from 220° to 253°C., measured on cristobalite samples made by heating quartz at various temperatures in the presence of various mineralizers. They suggest that the nature and amount of added substances may affect the inversion temperature. This foreign material may be taken to some degree into solid solution in the high cristobalite which forms during the firing operation. Evidence for this reaction is indicated by the close similarity of the crystal structure of high cristobalite, carnegieite, nepheline, and the feldspars. They also show that the temperature of inversion varies, depending not only on the temperature of formation but also on the mineralizer used in converting quartz to cristobalite.

The volume change has usually been measured indirectly by means of the linear expansion. The sample was in the form of grains or powder in the tests

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[2] T. F. W. Barth, "Cristobalite Structures: I, High Cristobalite," *Amer. Jour. Sci.*, **23** [136] 350–56 (1932); *Ceram. Abs.*, **12** [1] 20 (1933).

[3] T. F. W. Barth, "Cristobalite Structures: II, Low Cristobalite," *Amer. Jour. Sci.*, **24** [140] 97–110 (1932); *Ceram. Abs.*, **12** [1] 20–21 (1933).

[4] P. P. Ewald and C. Hermann, Strukturbericht, 1913–1928, p. 202. Akad. Verlags., Leipzig, 1931.

[5] C. Gottfried and F. Shossberger, Strukturbericht, Vol. III, 1933–1935, pp. 294–300. Akad. Verlags., Leipzig, 1937.

[6] Kurd Endell and R. Rieke, "Transformation of Silicic Anhydride at High Temperatures," *Tscherm. Mineral. Mitt.*, **31**, 508, 510 (1912).

[7] W. M. Cohn, "Problem of Heat Economy in the Ceramic Industry, II," *Jour. Amer. Ceram. Soc.*, **7** [6] 475–88 (1924); p. 487.

[8] R. H. H. Pierce, Jr., and J. B. Austin, "Comparison of Thermal Expansion of Used Silica Brick from Insulated and Uninsulated Open-Hearth Furnace Roof," *ibid.*, **19** [10] 276–87 (1936).

[9] R. B. Sosman, Properties of Silica, pp. 394–98. Amer. Chem. Soc. Monograph Series, No. 37; Chemical Catalog Co., New York, N. Y., 1927. 856 pp.; *Ceram. Abs.*, **7** [7] 505–506 (1928).

[10] N. W. Taylor and C.-Y. Lin, "Effect of Various Catalysts on Conversion of Quartz to Cristobalite and Tridymite at High Temperatures," *Jour. Amer. Ceram. Soc.*, **24** [2] 57–63 (1941).

[11] C. N. Fenner, "Stability Relations of Silica Minerals," *Amer. Jour. Sci.* [4th Series], **36**, 331–84 (1913).

[12] A. Q. Tool and Herbert Insley, "Crystalline Silica in Certain Devitrified Glasses," *Jour. Research Nat. Bur. Standards*, **21** [6] 743–72 (1938); RP 1152; *Ceram. Abs.*, **18** [3] 71 (1939).

[13] R. Weil, "Microscopic Study of Alpha-Beta Transformation of Natural Cristobalite," *Compt. Rend.*, **180**, 1949–51 (1935).

[14] S. Kondo and T. Yamauchi, "Inversion of Quartz to Tridymite, IX–X," *Jour. Soc. Chem. Ind. Japan*, **40** [Suppl. binding] 233 (1937).

[15] C. J. Van Nieuwenburg and H. J. Zijlstra, "Dilatometric Measurements on Tridymite and Cristobalite," *Rec. Trav. Chim.*, **47** [1] 1–12 (1928); in German, *Ber. Deut. Keram. Ges.*, **9** [4] 228–32 (1928); *Ceram. Abs.*, **7** [7] 457–58 (1928).

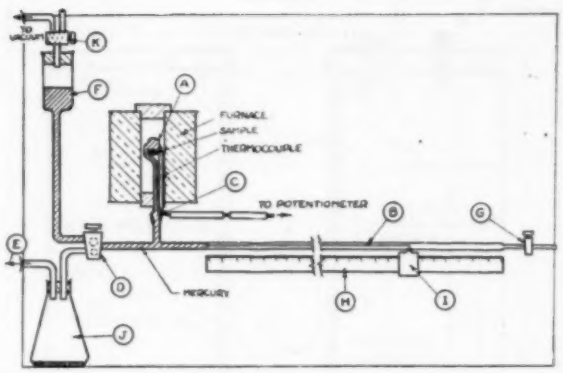

FIG. 1.—Diagram of apparatus.

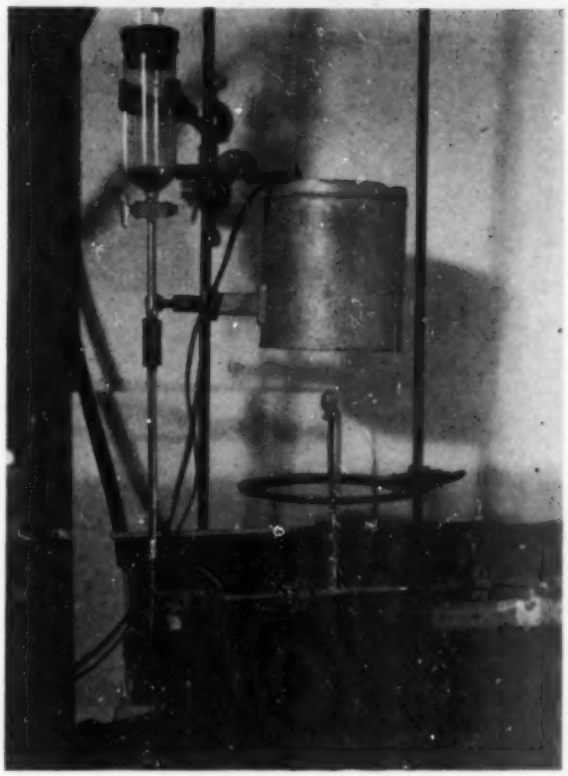

FIG. 2.—Dilatometer with furnace raised.

of Van Nieuwenburg and Zijlstra[15] and Lin[16] or in the form of tetrahedra in the interferometer measurements of Pierce and Austin.[8] Lin[16] gives the volume expansion in inversion as ranging from 0.6 to 2.3%.

Rigby, Dodd, White, and Green,[17] while investigating used silica brick which contained large amounts of cristobalite, found that the specimens showed a permanent expansion when heated up to 600°C. They state that this expansion appears to leave no doubt that the cristobalite inversion under certain conditions is not completely reversible but results in a permanent increase in the length of the specimen. They suggest, however, that this permanent expansion may be caused by other grains which do not return to their previous positions after being pushed apart by the expansion of the cristobalite; in other words, an increase in porosity occurs.

II. Apparatus

The true volume expansion can be obtained only when the solid material expands against itself. Each unit of the solid must be permitted to contribute its own change in volume to the total volume change. The objection to the indirect or linear expansion method of following the inversion is that the cristobalite is expanding in a porous system and the porosity could not be expected to be identical before and after expansion. Some of the grains would be expanding in free space and their volume change would not be registered.

To remove this objection, a dilatometer was constructed, wherein the finely powdered sample immersed in mercury expanded against a column of mercury. Thus, by subtracting the volume change of the immersion medium, the volume change of the solid could be obtained. The problem of insuring complete contact of the solid and immersion liquid is not easily solvable because of the microporosity of the sample. Since temperature placed a limitation on the choice of liquid, mercury was selected because it is liquid up to the top temperature of the test. Because of the high vapor pressure, it is not unreasonable to believe that the mercury would distill into the micropores; this might require some time and would be favored by the expansion attending the inversion. As will be seen later, this distillation quite possibly did occur.

The apparatus used to study the thermal expansion of cristobalite is shown in Figs. 1, 2, and 3.

A Pyrex-brand glass tube, *A*, of approximately 3-cc. capacity was connected to a capillary, *B*, by means of a ground glass joint, *C*, sealed with stopcock grease and cemented in place with G. E. Glyptal cement. The sample tube and capillary were also connected to a third section of tubing leading to a two-way stopcock, *D*. One of the outlets of stopcock *D* led to the vacuum pump (Cenco Megavac), *E*, while the other led to a mercury reservoir, *F*. This arrangement permitted the introduction of mercury into the evacuated system without destroying the vacuum. A second stopcock, *G*, was attached to the end of the capillary so that the system could be opened to the atmosphere. A standard meter stick, *H*, with a sliding pointer, *I*, was mounted parallel to the capillary. Between the system and the vacuum pump was placed a trap, *J*.

The furnace used in heating (Fig. 4) consisted of a $5^1/_2$-in. length of $1^1/_{16}$-in. inside diameter seamless steel

[16] C.-Y. Lin, "Effect of Various Catalysts on Conversion of Quartz to Cristobalite and Tridymite at High Temperatures." Thesis, Department of Ceramics, Pennsylvania State College, May, 1939.

[17] G. R. Rigby, A. E. Dodd, R. P. White, and A. T. Green, "Investigation of Permanent Expansion of Silica Products Containing Cristobalite," *Trans. Brit. Ceram. Soc.*, **42** [2] 11–20 (1943); *Ceram. Abs.*, **22** [6] 101 (1943).

FIG. 3.—Close-up of expansion bulb and thermocouple.

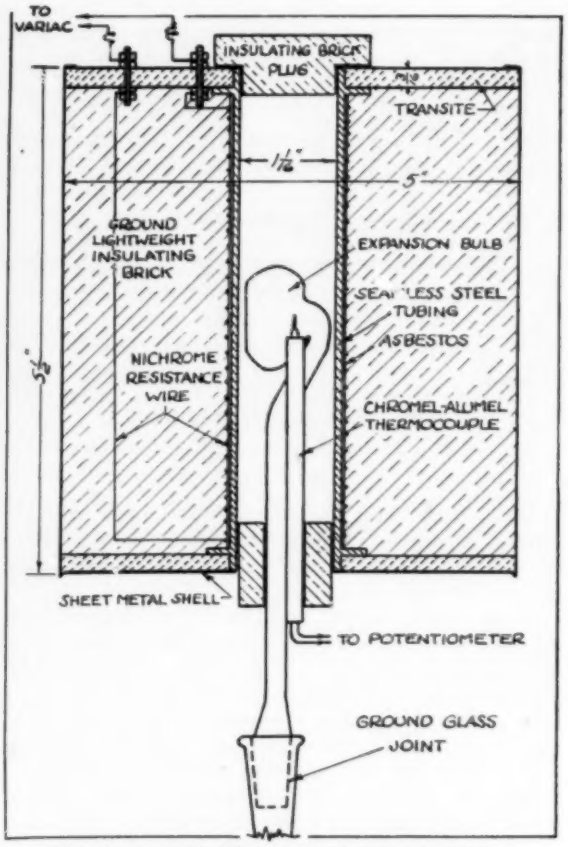

FIG. 4.—Detail of furnace and expansion bulb.

tubing wrapped in asbestos and wound with Nichrome B and S No. 27 resistance wire (eight turns per inch). This tube was mounted in a 5-in. diameter sheet-metal container. Two disks of $^3/_{16}$-in. Transite, 5 in. in diameter, formed the ends of the furnace. The space between the walls and the tubing was filled with crushed insulating brick. Two plugs of insulating brick were used to close the ends of the heating chamber.

The temperature was measured with a calibrated Chromel-Alumel thermocouple entering through the bottom (see Fig. 4); this thermocouple was calibrated against a Bureau of Standards calibrated couple. The hot junction of the thermocouple was placed in contact with the expansion bulb, midway between the top and bottom. Temperature was measured with a precision of $\pm^1/_2$°C.

Because the temperature was measured outside the expansion bulb, the actual temperature of the sample was probably slightly lower during heating and slightly higher during cooling. This temperature difference could not be determined, but it was kept at a minimum by maintaining a low rate of heating the sample.

A metal ring supporting the furnace from the bottom insured that the furnace position was maintained constant for different samples and also that the position of the furnace with respect to the bulb was fixed. The temperature distribution within the furnace chamber was checked and found to be constant to within $^1/_2$°C. over the length of the bulb.

A capillary was chosen so that its entire length would be used during the run. The bore was quite uniform and had an average diameter of 0.0554 cm. Carefully cleaned mercury was used throughout the tests.

The design of the sample bulb was arrived at after many trials. The bulb, as shown in Fig. 3, permits the evacuation without serious loss of the fine material, ready introduction of the mercury, and easy mixing of the mercury with the sample.

III. Experimental Procedure

(1) Assembly of Expansion Bulb and Sample

In making the expansion measurements, each sample was ground in an agate mortar to pass a 200-mesh screen. It was dried at least twelve hours at 110°C., and a weighed amount (0.960 ± 0.001 gm.) was placed in the expansion bulb.

The bulb was sealed into the system and heated at 300°C. under vacuum (approximately 3 mm. of mercury) for one hour. The sample and bulb were allowed to cool to 100° C. (still under vacuum), at which temperature mercury was introduced, filling the system completely. By creating a partial vacuum above the mercury in the reservoir and by opening the stopcock communicating with the atmosphere, the mercury could be forced back along the capillary. By closing the stopcock leading to the reservoir, the mercury column could be halted at any point.

(2) Procedure for Obtaining Heating and Cooling Curves

The expansion bulb containing cristobalite im-

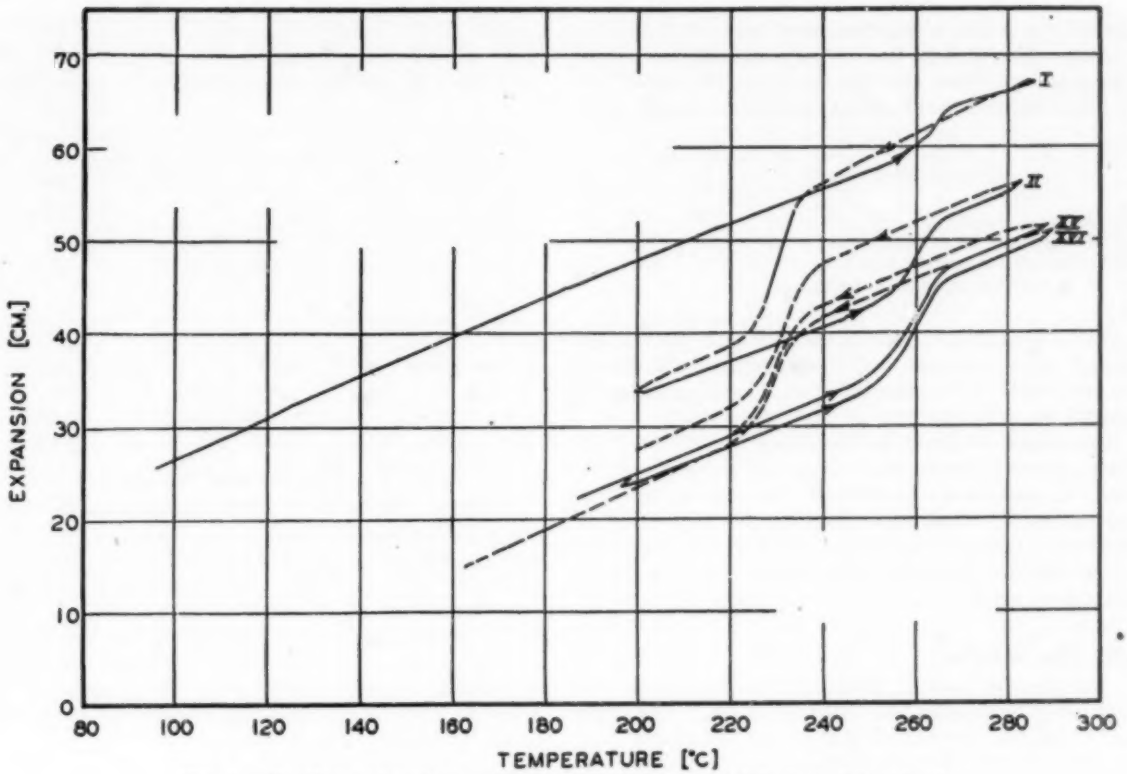

FIG. 5.—Heating and cooling cycles for sample No. 2; shrinkage undetermined.

	Cycle No.				
Heating	I	II	XV	XVI	Avg.
Initiation	261	255	254	254	254
Completion	266	265	265	265	265
Cooling					
Initiation	235	236	234	234	234
Completion	226	226	225	225	225

mersed in mercury was then heated at a rate of 3°C. per minute over the temperature range of 100° to 300°C. Temperature and expansion measurements were made at intervals of six degrees (two minutes), and at intervals of three degrees (one minute) during periods of rapid expansion.

When a temperature approaching 300°C. was reached (or after the inversion had occurred), the current through the resistance wire was decreased and the bulb was cooled at the same rate (3° per minute). After the bulb and sample had been prepared, as many cycles as desired could be run. An examination of the top of the bulb revealed when it was completely filled with mercury.

(3) Factors Pertaining to Expansion Measurements

(*A*) *Hysteresis Effect of Inversion:* The first cooling curve showed a greater apparent volume change during the inversion than did the first heating curve. During the second cycle, however, the volume change on heating increased slightly and the volume change on cooling decreased slightly, indicating that the two effects were approaching equality. After fifteen cycles, the two were nearly the same and a typical hysteresis curve resulted (see Fig. 5).

This "shrinkage" effect is believed to be the result of more complete penetration of the cristobalite mass by the mercury. When the mercury is first introduced, there is a certain amount of void existing between the grains or as micropores. As the inversion takes place, the grains shift positions slightly and possibly shatter, thus permitting penetration of the mercury into the previously occluded pores or cavities. If penetration occurs upon heating, the volume change will be apparently less than the true volume change; if it occurs upon cooling, the change will be apparently more.

During the experimental work, data were taken on the first and second cycles. Twelve complete cycles were run rapidly over the temperature range, 180° to 280°C., and data again were taken on the fifteenth and sixteenth cycles, when approximate equilibrium had been attained.

(*B*) *Determination of Inversion Temperature and Volume Change:* After equilibrium had been reached, the straight-line curve was extended past the point where the inversion occurred and the distance (indi-

cated by a in Fig. 6) was measured between it and the corresponding straight line resulting after expansion had taken place. From this measurement, the percentage volume change was calculated as shown in equation (1).

$$\text{Percentage volume change} = \frac{(a\pi d^2 D)100}{4W} \qquad (1)$$

a = linear expansion (cm.).
d = diameter of capillary (cm.).
W = weight of sample (gm.).
D = density of sample (gm./cc.).

The temperature at which the inversion started and ended was determined by extrapolation of the curves on either side of the point where rapid expansion began (points b and b', Fig. 6).

One cristobalite sample (No. 3) was run at three different rates of heating and cooling (3° per min., 5° per min., 7° per min.). A rate of 3°C. per minute was selected as the most convenient for use, although the three rates appeared to have no effect on the magnitude of the inversion or on the temperature at which the inversion occurred.

(4) The Samples

The samples used in these tests and their thermal and other properties are listed in Table I. Samples No. 1 and No. 3 were available in this laboratory from other researches. The other samples were prepared from the raw materials listed by firing pressed, bonded cakes of batch in a gas-fired furnace, the temperature of which was measured by means of an optical pyrometer. Alkali mineralizers were used as indicated in Table I. The purity of the samples was determined by means of an HF-evaporation. Duplicate density measurements, using water as the immersion medium, were made on each sample according to the usual laboratory procedures. The samples were examined microscopically. Cristobalite was the principal mineral in each sample, but each showed traces of tridymite and occasionally some residual quartz.

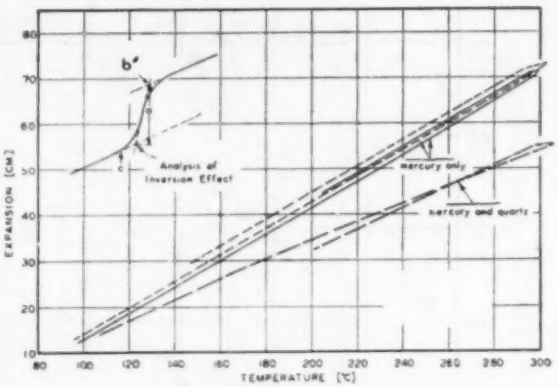

FIG. 6.—Base curves.

IV. Experimental Results

Reference curves (Fig. 6) were established by measuring the thermal expansion, first, with the bulb filled with mercury alone and then with the bulb filled with a weight of −200-mesh Brazilian quartz equal in volume to that of the cristobalite sample. In both cases, smooth, almost straight-line expansion curves were obtained; and in both cases with mercury alone, the cooling curves remained above but parallel to the heating curves, indicating some unanalyzed peculiarity of the dilatometer-liquid-solid system.

During heating, the interior of the bulb was slightly cooler than the temperature recorded by the thermocouple outside the bulb. The shape of the quartz-mercury curve on the instant of reversal from heating to cooling probably can be explained on the basis that at this instant the thermal gradient is at a minimum and later increases so that the cooling curve remains parallel to but above the heating curve. No data are available on the thermal gradient within the mercury itself (see Fig. 1 *B–C*). The ease of reproducibility of the reference curves favors the assumption that the gradient was constant for a cycle and did not respond to the normal changes in room temperature.

TABLE I

PROPERTIES OF TEST SAMPLES

Sample No.	Silica (source)	Mineralizer	Firing time	Firing temp.	Density of final product (gm./cc.)	Silica (%)
1	Pottery flint	Na^+	4 times	Cone 12	2.334	98.76
			Hr.	(°C.)		
2	Sample No. 1	2% CaO	24	1500	2.331	99.07
3	Oriskany sandstone	Na_2SiO_3		850–1050	2.346	95.98
4	Cold end of used silica brick A				2.332	93.8
5	Gray zone of brick A				2.446	87.0
6	Cold end of used silica brick B				2.314	93.3
7	Gray zone of used brick B				2.449	88.0
		Li_2CO_3 (%)				
A–1	Quartz rock crystal	1.5	4	1500	2.341	99.31
A–2	" " "	1.25	4	1550	2.340	99.68
A–3	" " "	1.00	4	1600	2.332	99.78
B–1	C.p. silicic acid	1.50	4	1500	2.329	99.36
B–2	" " "	1.25	4	1550	2.330	99.62
B–3	" " "	1.00	4	1600	2.328	99.76

Upon continued cooling, the cooling curve dropped below the heating curve, evidently because of better penetration of the mercury into the voids between the quartz grains.

Three preliminary curves were made, using sample No. 2 of three different grain sizes (−200-mesh, 100–200-mesh, and 65–100-mesh). At that time it was decided that the grain size of −200-mesh would be most suitable. Because cristobalite occurs essentially as very small crystals, the smaller the grain size the more likely it would be that each grain is a single crystal.

The data on the inversions for the various samples are given in Table II. The heating and cooling curves were plotted as expansion in centimeters of mercury versus temperature. The inversion temperature is defined in these curves, as in the work of Pierce and Austin,[8] as the temperature at which the change in slope appeared in the expansion curve (point *b*, Fig. 6). The writers used the average temperature obtained on four cycles (cycles I, II, XV, XVI). The variation between cycles was within the precision of temperature measurements. The temperature of completion of the inversion was determined by an extrapolation similar to the one for the initiation temperature.

The duration of the inversion is the temperature difference between temperature of initiation and completion. The percentage expansion was obtained according to formula (1). The change-of-length term in the formula was measured from the curve by taking the vertical distance corresponding to the duration of the inversion. The calculation of the percentage expansion assumes that the volume change of the mercury in the capillary (corrected for the straight-line thermal expansion of the mercury–cristobalite system) is equal to the volume change of the cristobalite during inversion. An identical procedure was used to obtain the data on the cooling curves. The hysteresis effect represents the difference between the mean temperature on the heating curve and the mean temperature on the cooling curve for any one run.

The expansion-temperature curve in Fig. 5 was selected as a typical curve for analysis.

From the point at which the expansion measurements start (approximately 90°C.) up to the initiation of the inversion, a straight-line relation exists between the linear expansion and temperature. There is a slight but hardly noticeable tendency for the slope of the line to decrease after a temperature of 200°C. is reached. At approximately 5° below the initiation of inversion (as determined by extrapolation), a slight increase in the slope (a "warning" effect) is noticed. As the temperature increases, the slope increases, reaches a maximum, then decreases to its previous value, and remains constant. The expansion-temperature curve is a straight line above and below the inversion temperatures and the two lines are essentially parallel.

The cooling curve follows the heating curve at temperatures above the low-high inversion temperature. As the sample is cooled below the temperature at which inversion is complete, the cooling curve continues as a straight line. At approximately 20°C. below the inversion temperature obtained on heating, inversion from high-to-low cristobalite begins and the cooling curve drops rapidly below the heating curve. There is no "warning" effect. The inversion continues over a small range of temperature after which the curve once more becomes a straight line, very nearly parallel to the straight line obtained above the inversion. The straight-line portions of the cooling curve show a slightly greater slope than those of the heating curve.

During the first cycle, the apparent volume change on cooling is about four times as great as the apparent volume change during heating. It is believed that this difference, as well as the greater slope of the cooling curve, is accounted for by more complete penetration of the powder mass by the mercury.

As cycle II is started, the heating curve remains below the cooling curve of cycle I. The heating curve of cycle II was the same as for cycle I except that the apparent volume change during inversion increased and the curve remained well below the curve of cycle I.

When the sample is cooled, the straight-line portion of the curve above the inversion temperature remains above, but parallel to, the straight-line portion of the

TABLE II

INVERSION DATA ON VARIOUS SAMPLES

Sample No.	Firing temp.	Heating: Initiation of inversion (°C.)	Heating: Completion of inversion (°C.)	Heating: Duration (°C.)	Heating: Expansion (%)	Cooling: Initiation of inversion (°C.)	Cooling: Completion of inversion (°C.)	Cooling: Duration (°C.)	Cooling: Volume change (%)	Hysteresis effect (°C.)
1	Cone 10 (°C.)	242	253	11	4.7	229	217	12	4.7	24.5
2	1500	254	265	11	5.3	234	225	9	5.3	30.0
3	850–1050	241	256	15	4.7	231	217	14	4.7	24.5
4	See Table I	223	235	12	1.4	214	204	10	1.4	19
5	" " "	253	271	18	3.0	234	223	11	3.0	30
6	" " "	233	246	13	0.9	221	215	6	0.9	18
7	" " "	252	265	13	3.4	232	221	11	3.7	31
A–1	1500	262	273	11	4.7	242	230	12	4.7	31
A–2	1550	263	273	10	6.2	242	231	11	6.2	32
A–3	1600	264	273	9	6.4	239	230	9	6.2	34
B–1	1500	260	268	8	7.0	239	229	10	7.0	30
B–2	1550	261	269	8	7.0	239	230	9	7.0	31
B–3	1600	262	272	10	6.4	239	229	10	6.4	33

heating curve obtained above the inversion temperature. This effect is explained by the fact that the exact temperature of the sample is not measured but rather the temperature on the outside of the expansion bulb. On heating, the temperature of the cristobalite–mercury system in the expansion bulb is slightly lower than the measured temperature, whereas on cooling it is slightly higher. Thus, for a measured temperature, the length of the mercury column while heating is in progress is slightly less than it is if cooling is taking place.

The same cooling curve is obtained as in cycle I, except that the apparent volume change on inversion is less; the straight-line portion of the curve at temperatures below inversion is still well below the straight-line portion of the heating curve but more nearly parallel.

Heating and cooling curves for cycles XV and XVI are similar in shape to the curves of cycle I; by this time, however, almost complete penetration and approximate equilibrium had been reached and a hysteresis loop had been attained. The heating curve for cycle XVI, however, is slightly below the heating curve for cycle XV, showing that there was still some penetration of the powder mass by the mercury. The "warning" effect as cristobalite inverted from the low to the high form is more noticeable, but there is little evidence of such an effect during the high-low inversion.

Several samples (Nos. 4 through 7) were taken from silica brick used in the roof of open-hearth furnaces. The cold ends of two silica brick (A and B) were represented by samples No. 4 and No. 6; the gray zone of the same two brick were represented by samples No. 5 and No. 7.

The temperature range was consistent in the four samples. The gray zones containing cristobalite, stabilized at a higher temperature, had a higher inversion temperature range and the cold end samples had a correspondingly lower temperature range. The volume expansion of the cristobalite in any sample of brick would probably be related to the amount of cristobalite present. The word "probably" is used in the last sentence to indicate some doubt as to the effect of mineral placement and size distribution of the cristobalite on the volume expansion. Assuming that quantity alone determines the amount of volume expansion, it can be assumed that the samples from the gray zone (No. 5 and No. 7) were predominantly cristobalite and that the "cool-end" samples (No. 4 and No. 6) contained much less cristobalite. Taking the ratios of the volume changes as a relative measure of the amounts present, the hot ends had approximately three times as much cristobalite as the cold ends.

This expansion technique thus can be used not only to estimate the temperature at which a particular brick has been fired or stabilized but also to obtain some idea of the cristobalite content. Additional work must be done on the volume aspect of the inversion to render the technique more precise.

The volume change calculated as percentage expansion is 7.0% in samples B–1, and B–2. Samples A–1, A–2, A–3 show a progressively greater volume change as firing temperature increases. Since inversion temperature is a function of firing temperature, there is a possibility that volume change is also dependent on firing temperature. It is more likely that the increase is due to more complete conversion of quartz to cristobalite, and a value of 7% or greater would be obtained if conversion were complete. Because the volume change for these samples approaches 7%, this figure would seem to be the volume change which occurs during the inversion of a sample consisting solely of cristobalite.

That such a magnitude is possible is indicated by the estimation of the volume change from the published lattice constants. Using the data from the structure work of various investigators,* the calculated volume change for the low-high inversion ranges from a value of 3.9 to 8.0%.

V. Conclusions

(1) The cristobalite inversion phenomenon has been shown to take place over a range of temperature and to exhibit a variable volume effect, depending on the origin, history, and composition of the samples.

(2) The inversion temperature varies in heating and cooling, the temperature on cooling being the lower. The temperature of the inversion appears to be closely related to the highest temperature at which the cristobalite was held for any length of time.

(3) The volume change on inversion is a function of the cristobalite present in the sample, possibly influenced by the temperature of formation, presence of added catalysts, and grain size. Shrinkage shown during heating and cooling cycles is due to gross structural adjustments within the sample, permitting the penetration of the mercury, but it may also be related to volume stabilization of the individual cristobalite units as a result of repeated disruption.

(5) The apparatus gives reproducible results and should be of value in estimating the cristobalite content of silica brick.

Acknowledgment

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* See footnotes 2, 3, 4, and 5.

CONVERSION OF CERTAIN REFRACTORY OXIDES TO A SUBOXIDE FORM AT HIGH TEMPERATURES*

By C. A. Zapffe

Abstract

A preliminary survey of the information published in the fields of chemistry and physics on the suboxide forms of SiO, TiO, ZrO, CrO, AlO, BO, VO, and CbO indicates a new field to be explored in determining the role of these suboxides in the service and failure of refractories and in the chemistry of slags. Several phenomena at the present time little understood, such as devitrification in reducing atmospheres, volatilization of refractory oxides, and certain slag types now classed as anomalous, may find their explanation in the decomposition of the oxides to low oxide forms under the favorable conditions of high temperature and low oxygen pressure which characterize much of their service.

I. Introduction

Silicon monoxide, SiO, is a high-temperature form of silica which has received all too little consideration by ceramists and metallurgists alike, although for years it has been identified and studied by other scientists. Other suboxides similarly have been identified and invite further attention; these include TiO, ZrO, AlO, VO, CrO, CbO, and BO.

These suboxides, which are difficult to study because they are high-temperature forms unstable at ordinary temperatures, merit no more neglect than do the similarly unstable high-temperature forms of quartz, tridymite, and cristobalite. Their importance in ceramic studies figures in their complete dependence on the seldom-controlled oxygen pressure, or activity, of the system being studied and on the fact that most of them have such high vapor pressures that they are virtually gases. Herein they may lead to confusion in imperfectly controlled tests because, as atmospheric conditions become more reducing or more oxidizing, the formation of the suboxide is aggravated or suppressed. They therefore impose a variable on the system which should be studied and controlled if research is to attain greater refinement.

In the first place, their frequently high volatility may effect a compositional change of the system; second, their production involves a chemical reaction, which is known to be important in the progress of such phenomena as recrystallization or devitrification; and third, they may have phase relationships of their own, which remain to be discovered.

Suboxide fayalites, sillimanites, chromites, etc., for example, are distinct possibilities remaining to be explored. They would represent refractory forms having insufficient oxygen at high temperatures to allow their orthodox constitution; such studies might throw light on the behavior of slags and furnace refractories in contact with liquid iron, whose oxygen pressure is favorably low and is often made lower by the addition of deoxidizing alloying elements.

Because most of the available information concerns the suboxide form of silicon, whose customary dioxide is one of the most frequently used refractories, the record on SiO will be examined.

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II. Conversion of Silica to Silicon Monoxide at High Temperature

(1) Discovery and Identification of SiO

In 1890, Winkler,[1] a chemist, postulated that the monoxide of Si should form from the reaction of Si with SiO_2 at high temperatures, but he was unsuccessful in producing it. In 1905, Potter[2] noticed a peculiar light condensate while working with the electric furnace; after analyzing the substance and finding it to correspond to the formula SiO, he patented a process for its manufacture and marketed the material under the trade name of Monox.* Its characteristics, he claimed, made it suitable for pigment, abrasive, or lubricant. Potter's product received considerable attention from contemporaries,[3] but it suffered the handicap of all such

[1] C. Winkler, "Reduction of Oxides by Magnesium," *Ber. Deut. Chem. Ges.*, **23**, 2642–68 (1890).

[2] (*a*) H. N. Potter, Fr. Pat. 360,875 (1905); Brit. Pat. 26,788 (1905); Ger. Pat. 182,082 (1905).
(*b*) H. N. Potter, "Method of Making Silicon Monoxid," U. S. Pat. 886,636 (1908); Brit. Pat. 1,279 (1906); Fr. Pat. 366,644 (1906); Ger. Pat. 189,833 (1905).
(*c*) H. N. Potter, "Monox," *Trans. Amer. Electrochem. Soc.*, **12**, 215–22 (1907).
(*d*) H. N. Potter, "Production of 'Monox,' New Electric Furnace Product," *ibid.*, **12**, 223–28 (1907).
(*e*) H. N. Potter, "Silicon Monoxide," *ibid.*, **12**, 191–214 (1907).
(*f*) H. N. Potter, "Process of Producing Silicon Monoxide," U. S. Pat. 1,104,384 (July 21, 1914).
* See footnotes 2(*a*), 2(*d*), and 2(*f*).

[3] (*a*) F. E. Lemaire, "Monoxide of Silicon," *Genie Civil*, **52**, 274 (1905).
(*b*) F. J. Tone, "Production of Silicon in Electric Furnace," *Trans. Amer. Electrochem. Soc.*, **7**, 243–49 (1905).
(*c*) A. B. Albro, "Analysis of Silicon Compounds," *ibid.*, **12**, 229–39 (1907).
(*d*) "Silicon Monoxide and Its Uses," *Engineering*, **85**, 722 (1908).
(*e*) F. Bock, "Several Innovations in Technical Utilization of Silica," *Chem. Ztg.*, **35**, 231–32 (1911).
(*f*) S. Hermann, "Innovations in Realm of Silicon Compounds," *Z. Electrochem.*, **17**, 190–92, 220–23, 250–53, 279–81 (1911).
(*g*) R. Flusin, "Silicon Monoxide and Oxycarbides, 'Monox and Fibrox,'" *Industrie Chimique*, **9**, 391–94 (1922).

(Footnotes 3(*h*) through (*j*) on p. 294.)

high-temperature forms in that it could not be examined at ordinary temperatures. Mere stoichiometry was not sufficient, opponents argued, to establish the material as SiO, inasmuch as it could conceivably be an intimate mixture of Si and SiO_2.

As a matter of fact, the material is often predominately a mixture of Si and SiO_2 at ordinary temperatures as shown by Baumann,[4] who used X-ray diffraction, and as may be seen in the photomicrograph of Fig. 1. This fact, however, should offer no more interference to accepting SiO as a high-temperature form than the analogous decomposition of FeO into Fe and Fe_3O_4.

Conclusive evidence for the existence of SiO first appeared in 1924 when Jevons [5] found the band spectra of SiO, and again in 1928, when he further verified its existence.[6] Bonhoeffer[7] then identified SiO spectrographically as a product of the reaction between C and SiO_2 at temperatures above 1500°C. In 1932, Saper[8] contributed the ultraviolet-band spectra of SiO, which were recently further studied by Woods.[9]

(2) Properties of SiO

Silicon monoxide generally occurs as a yellowish-brown condensate, often found in the cooler portions of the acid electric furnace when conditions have been strongly reducing. Its high volatility lends itself to powdering as the gas is rapidly cooled, although it is also found as a hard, vitreous condensate when cooled under certain conditions. "Silica snow," sometimes seen as a soft white deposit outside the furnace or as a dust escaping from a hot furnace, is apparently the result of SiO vapor coming in contact with air, which oxidizes it to finely divided SiO_2. The clever experiments of Biltz and Ehrlich[10] proved that such evidences for the evaporation of silicon can only be accounted for on the basis of SiO; SiO_2 shows no measurable evaporation whatever under oxidizing conditions; and metallic Si itself cannot attain a tenth of the observed volatility.

"Silox" was the SiO produced by the General Electric Company a quarter century ago.[11] A mixture

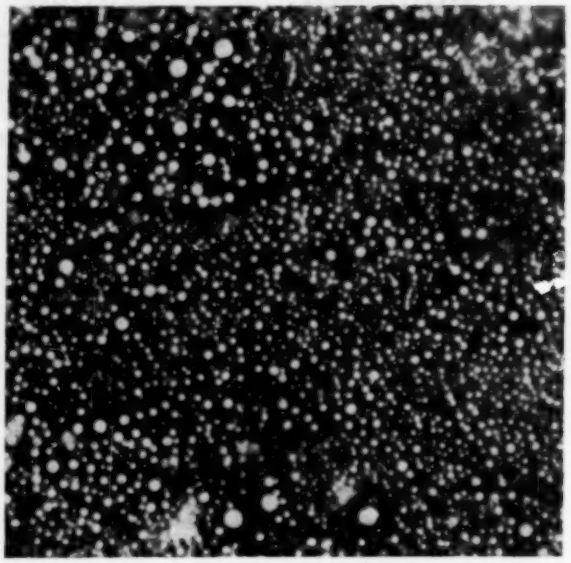

FIG. 1.—Photomicrograph of vitreous SiO residue showing decomposition products SiO_2 and Si, × 2000.

FIG. 2.—Powdery sublimate of SiO covering crater of arc struck underneath a mixture of sand and ferrosilicon, natural size.

(*h*) "Monoxide and Oxycarbides of Silicon," *Chem. Trade Jour.*, **71**, 445–46 (1922).

(*i*) J. W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. VI, Part 2, Carbon, Silicates. Longmans, Green & Co., London, 1925. 1024 pp.; *Ceram. Abs.*, **6** [4] 159 (1927).

(*j*) W. M. Latimer and J. H. Hildebrand, Reference Book of Inorganic Chemistry, 2d ed. Macmillan Co., New York, 1940. 563 pp.

[4] H. N. Baumann, Jr., "X-Ray Diffraction Examination of Material Having Composition SiO," *Trans. Amer. Electrochem. Soc.*, **80**, 95–98 (1941); *Ceram. Abs.*, **21** [10] 225 (1942).

[5] W. Jevons, "Band Spectra of Silicon Oxide and Chloride, and Chlorides of Carbon, Boron, and Aluminum," *Proc. Royal Soc.* [London], **106A**, 174–94 (1924).

[6] W. Jevons, "Ultraviolet Band-System of Carbon Monosulfide and Its Relation to Those of Carbon Monoxide (the '4th Positive' Bands) and Silicon Monoxide," *ibid.*, **117A**, 351–75 (1928).

[7] K. F. Bonhoeffer, "Existence of Gaseous Silicon Monoxide," *Z. Physik. Chem.*, **131**, 363–65 (1928).

[8] (*a*) P. G. Saper, "Ultraviolet Bands of SiO," [Series 2], *Phys. Rev.*, **40**, 465 (1932).

(*b*) P. G. Saper, "Rotational Analysis of Ultraviolet Bands of Silicon Monoxide," *ibid.*, **42**, 498–508 (1932); *Ceram. Abs.*, **12** [7] 279 (1933).

[9] L. H. Woods, "Silicon Oxide Bands," *Phys. Rev.*, **63** [11–12] 426–30 (1943); *Ceram. Abs.*, **22** [9] 164 (1943).

[10] W. Biltz and P. Ehrlich, "Volatilization of Silicon as Lower Oxide," *Naturwissenschaften*, **26**, 188 (1938).

[11] W. R. Whitney, General Electric Company, personal communication, January 31, 1941.

of sea sand and coke was fed into a closed brick arc furnace with a condensing chamber outside the building. The sand-coke mixture muffled the arc, giving a fairly constant energy input. At that temperature, and in the presence of the coke, the SiO_2 was reduced to SiO, which produced a fine, light condensate in the form of sheets suspended from the ceiling of the outside chamber. These sheets resembled an elephant's ear so much in color and shape that the name was applied by the men in the shop.[11]

Silicon monoxide can be prepared very simply by using a block of graphite for a ground and a welding electrode to make an arc. With the arc well covered with a sand-graphite mixture, SiO will be formed and can be cooled in a vessel inverted over the electrode. The reduction can be made (1) with carbon, $SiO_2 + C = SiO + CO$, or (2) with silicon carbide, $SiO_2 + SiC = SiO + CO + Si$. Silicon itself can act on carbon monoxide as (3) $Si + CO = SiO + C$; or, according to Mellor[3(f)] the oxycarbide may be formed as (4) $Si + CO = SiOC$. The proportion of silica and carbon in the mixture does not influence the composition of the final product, but the yield depends on the proportion of the initial materials. The specific gravity of SiO is listed by Mellor[3(f)] as 2.24, and its apparent specific gravity as 2.04.

(3) Uses of SiO

Among the most interesting of the experiments with SiO are those of Zintl and his colleagues,[12] which culminated in two patents.* They showed, first, that the SiO reaction could be used to remove SiO_2 from clays, slags, and refractories by adding powdered Si in stoichiometric quantities to the material and heating the mixture to temperatures between 1250° and 1450°C. *in vacuo*. The Si reacts with the SiO_2 in the material to form gaseous SiO, which escapes. Reaction (1) shows this type; only traces of Si or SiO_2 remain. They also list reactions (2) to (6) as examples.

$$(Me_xO_y)\cdot(SiO_2)_n + n\mathrm{Si} = Me_xO_y + 2n\mathrm{SiO} \quad (1)$$

$$(Al_2O_3)\cdot(SiO_2)_2 + 2\mathrm{Si} \rightarrow Al_2O_3 + 4\mathrm{SiO} \quad (2)$$

$$(BeO)_3\cdot(Al_2O_3)\cdot(SiO_2)_6 + 6\mathrm{Si} \rightarrow (BeO)_3\cdot(Al_2O_3) + 12\mathrm{SiO} \quad (3)$$

$$(ZrO)_2\cdot(SiO_2) + \mathrm{Si} \rightarrow ZrO_2 + 2\mathrm{SiO} \quad (4)$$

$$(Al_2O_3)\cdot(SiO_2)_2 + 2\mathrm{C} \rightarrow Al_2O_3 + 2\mathrm{CO} + 2\mathrm{SiO} \quad (5)$$

$$Cb_2O_5 + 5\mathrm{Si} \rightarrow 2\mathrm{Cb} + 5\mathrm{SiO} \quad (6)$$

In the second patent, Zintl and Grube[12(c)] used SiO as a reducing agent for recovering other metals from their oxide vapors as shown by reaction (7).

Burned dolomite heated with burned lime and SiO *in vacuo* at 1350°C. yielded a 99% distillation of magnesium in two hours (reaction (8)).

Zinc oxide likewise yielded 98% of its zinc in one hour at 1300°C. (reaction (9)).

$$Me_xO_y + y\mathrm{SiO} = x\mathrm{Me} + y\mathrm{SiO_2} \quad (7)$$

$$(MgO)\cdot(CaO) + \mathrm{CaO} + \mathrm{SiO} = Ca_2SiO_4 + \mathrm{Mg} \quad (8)$$

$$\mathrm{ZnO} + 2\mathrm{CaO} + \mathrm{SiO} = Ca_2SiO_4 + \mathrm{Zn} \quad (9)$$

(4) Experiments to Produce SiO

Although this paper is primarily an introductory review, calling attention to a new field for research, some preliminary experimentation is mentioned.

From silica sand mixed with granulated 75% FeSi, the sublimate shown in Fig. 2 was obtained. An arc was struck underneath the mixture by passing a graphite electrode through the bottom of an inverted crucible until contact was made with the graphite base. The atmosphere within the crucible soon excludes free oxygen, permitting SiO to remain unoxidized. The entire inside of the crucible becomes covered with fluffy, sublimed SiO. The SiO may deposit in a vitreous condition in the hot zone, whereas in the cooler zone, the sublimation usually results in the powder. Figure 2 shows the powdery material making a weblike covering over the crater built by the arc, the structure comprising the original sand-metal mix in progressive degrees of sintering, fluxing, and reduction.

According to Mellor,[3(f)] the reaction between silica and silicon is energetic at 1800°C. In a series of experiments of the foregoing type, the writer found that the gasifying reaction becomes increasingly rapid as the temperature is raised and, at some temperature beyond the range of the optical pyrometer (3300°F.), becomes near violent. By using a $^3/_8$-in. electrode and about 7 kw. of current, the temperature within the crucible became so great that the reaction was no longer restricted to the arc. The "blow" through the electrode port in the crucible bottom, moreover, was considerably more violent with a C-SiO_2 mix than with a FeSi-SiO_2 mix, probably because a second gaseous product, CO, is also produced.

Depending on the ratio of Si to SiO_2, a metallic residue may form beneath the arc. The slag in such cases shows some unusual characteristics (these will not be reported at this time). The Si content of the metal button is considerably less than the Si content of the FeSi, showing that Si has been lost simultaneously with the removal of SiO_2 by reaction (10).

$$(\mathrm{Fe})\mathrm{Si} + \mathrm{SiO_2} = 2\mathrm{SiO}\ (+\ \mathrm{Fe}) \quad (10)$$

III. Conversion of Other Oxides

Similar conversion of other oxides to lower forms has been established for almost every commonly used oxide, although their study in most cases is considerably less developed than that of SiO. Their chemistry is identical, however, the existence of each depending on high temperature and low oxygen pressure, commonly spoken of as "reducing conditions." Since both these factors are common to many uses of re-

[12] (*a*) E. Zintl, W. Bräuning, H. L. Grube, W. Krings, and W. Morawietz, "Silicon Monoxide," *Z. Anorg. Allgem. Chem.*, **245**, 1–7 (1940).
(*b*) E. Zintl, W. Krings, and W. Bräuning, "Process of Removing Silica from Minerals, Slags, and Similar Materials," U. S. Pat. 2,242,497 (May 20, 1941); *Ceram. Abs.*, **20** [7] 184 (1941).
(*c*) E. Zintl and H. Grube, "Reduction of Inorganic Oxidic Compounds by Silicon Monoxide," U. S. Pat. 2,286,663 (June 16, 1942).
* See footnotes 12 (*b*) and 12 (*c*).

fractories, recognition of these suboxide forms seems warranted.

In the present paper, only those suboxides are considered which are monoxides, formula type XO, because they appear to be a predominating group, at least among recognized suboxide forms. Other types also exist, of course, and may later be shown to be as important.

Some of these monoxides have been identified and described as follows:

FeO and MnO, accepted forms.
SiO (footnotes 1–12 and 21).
CrO (Dieckmann,* Granat,† and footnotes 13–18 and 20.)
TiO (Kreimer‡).
VO (footnotes 13 and 25).
BO (footnotes 22 and 24).
AlO, ZrO, and PO (footnote 24).
CbO (also Cb_2O) (footnote 26).

(1) CrO

Next to SiO, CrO has received the most attention. Ferguson[13] and Ghosh,[14] among others, have carefully studied the band spectra of CrO. Slade and Higson[15] measured the CO pressures in equilibrium (11).

$$5Cr + CO = Cr_4C + CrO \quad (11)$$

Körber and Oelsen[16] and Löfquist[17] studied CrO as a component of slags and inclusions in chromium steels.

The investigations of Löfquist are especially interesting. He identified a slag inclusion in steel as a CrS–CrO eutectic; whereas Körber and Oelsen proved that chromium does not oxidize simply to Cr_2O_3 in the slag but exists from 40 to 100% as CrO, depending on the oxygen activity of the system as determined by Mn, Si, and Cr. They then showed that chromous oxide silicates, $(CrO)_x(SiO_2)_y$, are very fusible in contrast to the immiscible Cr_2O_3–SiO_2 system and that, on slow cooling, the suboxide slag decomposes with concomitant crystallization and precipitation of metallic particles. The analogy here to the Si–O system is marked. These observations suggest intriguing new fields for research on slags, inclusions, and refractories.

Maier[18] provides a rigorous discussion of CrO and some useful data. His calculation of the specific heat of CrO is given in equation (12).

$$C_p = 13.07 + 4.0 \times 10^{-3}\,\theta - 1.07 \times 10^{-1}\,\theta^2 \quad (12)$$

In equation (12), θ is a simplified designation for high temperatures, θ = °K. − 1000°. The first term is the actual specific heat at 1000°K., and the coefficient of the second term is the slope of the curve of specific heat versus temperature at 1000°K. Then, considering reaction (13) and the data from a research by Heusler,[19]

$$Cr_2O_3 + C = 2CrO + CO \quad (13)$$

Maier calculates ΔC_p and the sigma function for the C–Cr_2O_3 equilibrium at various temperatures and CO pressures, from which he obtains the thermodynamic functions (14), (15), and (16).

$$\Delta H_{o_\theta} = 51{,}400, \quad I = 19.16 \quad (14)$$

$$\frac{\Delta F_T}{T} = \frac{49.08 \times 1000}{T} - 2.34\,lnT - 0.08 \times 10^{-3}\,T + 0.05 \times 10^{-6}T^2 - 19.16 \quad (15)$$

$$\Delta F_{o_\theta} = +13{,}720 \quad (16)$$

Thus, at 1000°K. (727°C.), the reaction lies well toward Cr_2O_3 but proceeds toward CrO with increasing temperature. Maier similarly develops reaction (17) for the synthesis of CrO with the values shown in (18), (19), and (20).

$$Cr + {}^1/_2O_2 = CrO \quad (17)$$

$$\Delta H_{o_\theta} = -94{,}545, \quad S_{o_\theta}\,(CrO) = 20.08 \quad (18)$$

$$\Delta F_{o_\theta} = -71{,}707 \quad (19)$$

$$\frac{\Delta F_T}{T} = -95.49 \times \frac{1000}{T} - 0.65\,lnT - 0.23 \times 10^{-3}T - 0.04 \times 10^{-6}T^2 + 29.54 \quad (20)$$

These values show that CrO tends to be produced from Cr and O_2 with vigor even at 727°C., although no conclusions can be drawn regarding its stability in air, for example, because of subsequent oxidation to Cr_2O_3.

The principal significance of these values lies in showing the relationship of CrO with the so-called "reducing conditions" of furnace atmospheres. Thus, when the oxygen pressure, measurable as P_{CO} in certain carboniferous atmospheres, becomes very low, the development of CrO may considerably affect a refractory system, such as chromite brick, having Cr_2O_3 as a constituent. Two reactions between the carbide and oxide of Cr also of interest[20] are shown in (21) and (22).§

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* T. Dieckmann and O. Hanf, "Notice on Chromous Oxide," *Z. Anorg. Allgem. Chem.*, **86**, 301 (1914).

† I. Y. Granat, "Reduction of Chromium Oxide," *Metallurg*, **11** [10] 35–41 (1936).

‡ G. S. Kreimer, "Simultaneous Reduction of Oxides of Iron, Titanium, and Columbium with Aluminum," *Jour. Applied Chem.* [U. S. S. R.], **13**, 1267–70; in French, p. 1271 (1940).

[13] W. F. C. Ferguson, "Chromium Oxide and Vanadium Oxide Band Spectra," *Bur. Stand. Jour. Research*, **8** [3] 381–84 (1932); RP 423; *Ceram. Abs.*, **11** [6] 391 (1932).

[14] C. Ghosh, "Band Spectrum of Chromium Oxide," *Z. Physik*, **78**, 521–26 (1932).

[15] R. E. Slade and G. I. Higson, "Equilibria in Reduction of Oxides by Carbon," *Jour. Chem. Soc.* [London], **115**, 205–14 (1919).

[16] F. Körber and W. Oelsen, "Reactions of Chromium with Acid Slags," *Mitt. Kaiser-Wilhelm Inst. Eisenforsch. Düsseldorf*, **17**, 231–45 (1935).

[17] H. Löfquist, "Microscopic Studies on Slag Inclusions in Iron and Steel," *Jernkontorets Ann.*, **117**, 49–111 (1933).

[18] C. G. Maier, "Sponge Chromium," *U. S. Bur. Mines Bull.*, No. 436, 109 pp. (1942).

[19] O. Heusler, "Remarks on Equilibrium During Reduction of Chromium Sesquioxide and Uranium Dioxide by Means of Carbon and Effect of Nitrogen on Uranium Carbide," *Z. Anorg. Allgem. Chem.*, **154**, 353–74 (1926).

[20] O. Meyer, "Course of Reactions Between Graphite and Oxides, Especially Between Heavy Metallic Carbides and Oxide," *Arch. Eisenhüttenw.*, **4**, 193–98 (1930); see also footnote 18.

§ A recent article by F. S. Boericke, "Equilibria in Reduction of Chromic Oxide by Carbon, and Their Relation to Decarburization of Chromium and Ferrochrome," *Bur. Mines Rept. Invest.*, No. 3747, 34 pp. (1944), is not in agreement with these reactions.

Hydrogeniferous atmospheres similarly may reduce the oxygen pressure to values where CrO is produced. Maier lists two reactions which, taken together, depict the same stepwise reduction equilibria that were obtained for the reduction of SiO_2 in the presence of liquid steel[21] (reactions (23) to (26)).

$$5Cr_3C_2 + 4Cr_2O_3 = 3Cr_3C_4 + 4CO + 8CrO \quad (21)$$

$$Cr_3C_2 + 5Cr_2O_3 = 2CO + 13CrO \quad (22)$$

$$Cr_2O_3 + H_2 = 2CrO + H_2O \quad (23)$$

$$\frac{\Delta F}{T} = 22.74 \times \frac{1000}{T} + 5.80\, lnT - 2.40 \times 10^{-3}\, T + 0.23 \times 10^{-6} T^2 - 44.99 \quad (24)$$

$$CrO + H_2 = Cr + H_2O \quad (25)$$

$$\frac{\Delta F}{T} = 38.33 \times \frac{1000}{T} - 3.99\, lnT - 1.22 \times 10^{-3} T + 0.12 \times 10^{-6} T^2 - 39.08 \quad (26)$$

At the steelmaking temperature of 1600°C., for example, Maier finds P_{H_2O}/P_{H_2} to be 0.25 and 0.008, respectively, for the reduction of Cr_2O_3 to CrO and of CrO to metallic Cr. A hydrogeniferous atmosphere containing less than 19 mm. of water vapor (dew point, 21.3°C.) will therefore favor the production of CrO. To reduce CrO to Cr metal would require reducing the H_2O content of H_2 to 6 mm. (dew point, 4°C.).

By referring to the equilibrium for Si in steel,[21(a)] liquid steel at 1600°C. containing about 0.20 weight % of Si has an oxygen pressure equal to that of an atmosphere whose ratio P_{H_2O}/P_{H_2} is equal to 0.025. Such steel, consequently, should reduce the Cr_2O_3 in refractories to CrO at the slag-metal interface. Experience confirms this, for 0.20% Si in steel will reduce 10 to 20% Cr from a slag containing chromium oxide, and the slag analysis will approach 50% CrO.[16] The presence of other deoxidizing elements in steel, such as C and Al, makes the oxygen pressures being considered here a commonplace. Ceramists and mineralogists alike, however, seem to have given these complicating suboxide factors little consideration.

(2) BO, AlO, ZrO, VO, CbO, CbO_2

As for other suboxide forms, boron monoxide has been recognized since its spectrographic identification by Mulliken[22] twenty years ago. Since then it has been experimented with at some length by Wiberg[23] and by Zintl, Morawietz, and Gastinger,[24] and others; Zintl mixed boron with its sesquioxide and obtained the monoxide indicated in reaction (27). Mixing boron with alumina caused both B and Al to vaporize as monoxides (reaction (28)). When ZrO_2 was tried, however, only BO vaporized, leaving a residue whose analysis corresponded to ZrO.

$$B_2O_3 + B = 3BO \text{ (vapor)} \quad (27)$$

$$Al_2O_3 + B = 2AlO + BO \quad (28)$$

The band spectra of vanadium monoxide were studied by Ferguson,[13] and their crystal structure (FCC) was determined and measured by Klemm and Grimm.[25] As in the case of most of these high-temperature forms, VO decomposes on cooling to a mixture of V or a solution of O in V with a higher oxide. For the oxides of columbium, Brauer[26] has reported both CbO and CbO_2 and has determined and measured the crystal structure of CbO (FCC).

IV. Significance of Suboxides in Study of Refractories and Slags

The strong effect of "reducing conditions" on refractories is generally well known. Badger[27] found that H_2 increased vitrification even at 1170°C.; in discussing Dodd's paper,[28] Threfall states,

> Our experiences over a period of years in the manufacture of fire-clay brick is that hydrogen can be blamed for many failures, although I cannot point to any definite case where we have proof. But the indications undoubtedly are that hydrogen, especially on its formation, is an exceedingly active—one may even say virulent—reducing agent; and, if other conditions are suitable, may cause slagging of fire-clay refractories at temperatures as low as 500°C.

Dodd points out that the problem provoking his research on the deterioration of silica brick was the premature failure of the roof of an open-hearth furnace using pure coke-oven gas, a highly reducing mixture that is both carboniferous and hydrogeniferous, and that the failure was not merely a matter of "burning down." This again points to the possible formation of SiO. Dodd's statement, furthermore, that the failure was intimately connected with the working of the furnace is significant because the "working of a furnace" implies handling the reducing-oxidizing factors. A furnace operated on the reducing side would favor the formation of monoxides.

Zschacke[29] points to the amorphous silica found in the regenerator chambers and conduits of glassmelting

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[21] (*a*) C. A. Zapffe and C. E. Sims, "Silicon-Oxygen Equilibria in Liquid Iron," *Metals Tech.*, **9**, No. 6, 30 pp. (1942) [*Tech. Pub.*, No. 1498]; *Trans. Amer. Inst. Mining Met. Engrs., Iron & Steel Div.*, **154**, 192–227 (1943).

(*b*) C. A. Zapffe and C. E. Sims, "Silicon Monoxide," *Iron Age*, **149** [4] 29–31; [5] 34–39 (1942).

[22] R. S. Mulliken, "Isotope Effect of Band Spectra, I," *Phys. Rev.*, **25**, 119–38 (1925); "II, Spectrum of Boron Monoxide," *ibid.*, pp. 259–94.

[23] E. Wiberg, " 'Borohydrates' and Boron Suboxides of Travers, Ray, and Gupta," *Z. Anorg. Allgem. Chem.*, **191**, 49–59 (1930).

[24] E. Zintl, W. Morawietz, and E. Gastinger, "Boron Monoxide," *ibid.*, **245**, 8–11 (1940).

[25] W. Klemm and L. Grimm, "Lower Vanadium Oxides," *Z. Anorg. Allgem. Chem.*, **250**, 42–55 (1942).

[26] G. Brauer, "Oxides of Columbium," *Naturwissenschaften*, **28**, 30 (1940).

[27] A. E. Badger, "Effect of Various Gaseous Atmospheres on Vitrification of Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **16** [2] 107–17 (1933).

[28] A. E. Dodd, "Action of Water Vapour on Silica Brick at High Temperatures and Its Possible Industrial Significance," *Trans. Ceram. Soc.* [England], **35** [5] 223–46 (1936); *Ceram. Abs.*, **16** [7] 206 (1937).

[29] (*a*) F. H. Zschacke, "Deposits in Heat Regenerators and Waste-Gas Channels of Glassmelting Furnaces," *Sprechsaal*, **63** [11] 192–94; [12] 210–12; [13] 247–50 (1930); *Ceram. Abs.*, **9** [7] 518 (1930).

(*b*) F. H. Zschacke, "Volatilization of Components of Glass During Melting and Fining," *Glashütte*, **59**, 331 (1929); *Ceram. Abs.*, **8** [6] 648 (1929).

furnaces as an evidence of volatilization caused by hydrogen; and Sosman[30] records several of the foregoing observations, with many others, whose explanation may very well lie in the formation of SiO.[21(b)]

In a recent research by the writer on oxygen-silicon equilibrium in liquid steel,[21(a)] devitrification of the SiO_2 crucibles was found to depend in rate on the H_2O/H_2 ratio of the atmosphere, increasing as the proportion of H_2 increased. Crystallization, moreover, always proceeded from the surface and worked inward, an observation which Sosman[30] states is general. It must therefore be assumed that H_2 creates some subtle surface change, such as forming a thin film of SiO, which, perhaps upon subsequent decomposition, may introduce the nuclei that lead to crystallization. Inasmuch as SiO seems never to have been considered in relation to devitrification, some interesting new studies suggest themselves. Körber and Oelsen[16] found crystallization of chromium silicates to be coincident with metallic precipitation from a suboxide reaction.

Anomalous refractory forms have occasionally been observed among the brickwork of steelmaking furnaces since Percy[31] and Blair[32] discussed the siliceous aggregate (found eighty years ago) between the iron and the brickwork of a blast furnace, a substance which reacted with water to produce a gas that burned with a blue flame; SiO shows the same reaction.[3(f)]

As for other materials, the same fields remain to be explored. Among the slags and refractories that might form known suboxide systems when serving under conditions of sufficiently low oxygen pressure and high temperature are those normally containing Cr_2O_3, Al_2O_3, SiO_2, TiO_2, ZrO_2, B_2O_3, P_2O_5, and others. In some cases, a bulk phase may be found, having specific characteristics; the suboxide, in some cases, may simply affect the properties or the behavior of the original phase by altering it chemically or physically.

V. Conclusions

From the foregoing study, the following conclusions may be drawn: (1) SiO, CrO, BO, TiO, AlO, VO, CbO, CbO_2, and PO are suboxide forms whose identities have been rather securely established by chemists and physicists but which have received scant attention by ceramists, metallurgists, or mineralogists in studying the behavior of slags and refractories.

(2) Since conditions of high-temperature and low-oxygen pressure, conditions characterizing steelmaking furnaces, are conducive to the formation of suboxides, their study seems warranted. The present paper serves to introduce the subject with a preliminary survey.

(3) Suboxide forms may be used to clarify discrepant data and to explain certain behaviorisms of slags and refractories which at present seem anomalous.

(4) The high-temperature chemistry of suboxide phases is not clear. New phases might be found, such as suboxide fayalites, sillimanites, and chromites; and secondary effects on established phases may be found, such as devitrification nucleated by the chemical action or deterioration effected by the escape of the often volatile suboxide.

Acknowledgment

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[30] R. B. Sosman, Properties of Silica. Amer. Chem. Soc. Monograph Series, No. 37; New York Chemical Catalog Co., New York, 1927. 856 pp.; *Ceram. Abs.*, **7** [7] 505–506 (1928).

[31] J. Percy, "President's Address," *Jour. Iron Steel Inst.* [London], **29**, 8–31 (1886).

[32] T. Blair, "Certain Accessory Products of Blast Furnaces," *ibid.*, **29**, 81–87 (1886).

PROPERTIES OF SOME VYCOR-BRAND GLASSES*

By Martin E. Nordberg

Abstract

Physical and chemical properties are discussed for Vycor-brand 96% silica glasses prepared from glasses of lower silica content by a leaching process, and a brief résumé of this process is given. The intermediate porous glass and a translucent or white opaque form of the final 96% silica glass made by the Multiform process are briefly described. Ultraviolet and infrared transmission characteristics of glasses No. 790 and No. 791 are given.

I. Introduction

During the past four years, a group of very low-expansion glasses has been sold on the market under the trademark, Vycor. It is the purpose of this paper to discuss some physical and chemical properties of those glasses in the low-expansion group which are prepared by a unique method involving leaching and refiring. These glasses have been called "reconstructed" or "96% silica" glass. The first name is derived from the fact that such a glass is made from another glass; the second refers, of course, to the composition.

II. Process

(1) Initial Fabrication and Leaching

The process by which these glasses are made will be briefly described. An alkali-borosilicate glass is melted in a crucible, pot, or tank in the conventional manner and is then pressed, drawn, or blown to the desired but oversize shape. The resultant article, after finishing by such operations as cutting, grinding, and flameworking if necessary, is subjected to a heat-treatment at a temperature above the annealing point but below that which would give serious deformation. During this heat-treatment, the glass separates into two phases as evidenced by the gradual development of opalescence resulting from light scattering. These phases remain closely intermingled and can be considered, for practical purposes, continuous; since it has not been possible to detect any crystal formation, either microscopically or by X-ray methods even after prolonged heat-treatments, the writer believes that both are glassy.

One phase is rich in boric oxide and is soluble, particularly in acids; the other is high in silica and stable toward acids. It is possible to leach out the unstable portion of the glass, leaving a porous structure of very high silica content, and this is done by immersing the ware in a hot dilute solution of an acid. After this treatment, the porous glass is washed to remove the boric acid and salts in solution within the pores and is set aside to dry. In order for this process to be practical, the leaching must take place in reasonable time and the article must remain whole. Both of these requirements limit the choice of the parent glass to a narrow range of compositions, and the latter one necessitates close control in all steps of the process; even so, a thickness of about 8 mm. is considered to be the upper practicable limit for most purposes.

(2) Properties of Porous Glass

Inasmuch as the porous intermediate glass is new, differing from previous material of this type in that it can be produced in a variety of shapes, a few of its properties will be discussed. Some of these properties may suggest uses as semipermeable membranes, ultrafilters, catalyst carriers, and adsorbents.

It is but slightly opalescent in the wet state. It passes through an intermediate white opaque stage while drying and then partially clears again, but it remains more opalescent than when it is wet. On standing, it turns a yellow-to-brown color as a result of adsorption of organic matter from the atmosphere; when it is heated, this organic matter will char and the glass may even become black. The glass at saturation holds about 25% of water on the basis of its ignited weight, and it still retains from 3 to 6% when it is dried at room temperature over sulfuric acid or phosphorus pentoxide. The strength is relatively high; articles of the porous glass can therefore be handled in about the same way as a regular glass. The porous nature of the glass results in a tacky feel.

Emmett[1] has studied the adsorption of nitrogen near its boiling point by porous glass. The volume of nitrogen at standard temperature and pressure adsorbed per gram of porous glass at 79°K. is given as a function of the relative pressure, P/P_0, in Fig. 1, where P is the pressure of nitrogen above the sample and P_0 is the vapor pressure of liquid nitrogen. The solid line gives adsorption with increasing P/P_0 and the broken line with decreasing P/P_0.

The first rapid rise in the curve represents mainly the formation of a monomolecular layer of the nitrogen molecules on the walls of the pores. This is followed by the long, straight portion over which multimolecular layers are built up. Capillary condensation accounts for the next steep portion, and the fact that this process is complete at $P/P_0 = 0.9$ indicates that there are no large pores in the glass. The desorption curve coincides with that for adsorption except in the region

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 4, 1944 (Glass Division). Received May 1, 1944.

[1] P. H. Emmett, "Measurement of Surface Areas of Finely Divided or Porous Solids by Low-Temperature Adsorption Isotherms," in Advances in Colloid Science, Vol. I, pp. 1–36. Interscience Publishers, Inc., New York, 1942.

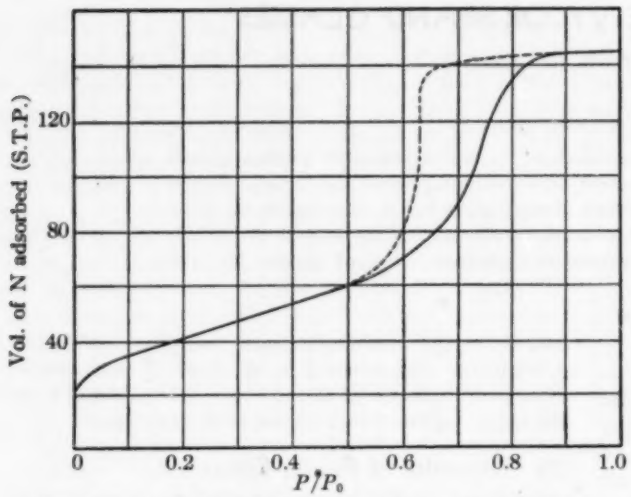

FIG. 1.—Adsorption of nitrogen on porous glass at 79°K.

of capillary condensation, where a considerable hysteresis effect is observed.

Emmett and DeWitt[2] later published adsorption data for nitrogen, oxygen, argon, butane, and carbon dioxide. Curves similar to Fig. 1 were found for all of the gases except carbon dioxide, which showed a relatively high adsorption at low values of P/P_0 and no rapid rise from capillary condensation up to $P/P_0 = 0.73$. This difference in the nature of adsorption as compared to that of the other gases was attributed to the fact that the carbon dioxide condenses to a solid whereas the other gases condense to liquids. From the early portion of the nitrogen-adsorption curve and using an equation developed by Brunauer, Emmett, and Teller[3] for multimolecular adsorption, they calculated a surface area of 121 sq. m. per gm. of glass. The volume of liquid nitrogen adsorbed at saturation was 0.18 cc. per gm. Assuming that the pores are cylindrical and the density of the condensed nitrogen is the same as that of the normal liquid, an average pore radius of 30 a.u. was calculated. Similar calculations were made for other gases, and the radius was also calculated in various ways from the capillary condensation. Details will not be given here except that the largest pore radius was found to be 60 a.u.

If a density of 2.18 gm. per cc. is assumed for the solid portion of the porous structure, the void space can be determined. It amounts to about 28% of the total volume. The fact that this is lower than the over-all shrinkage on firing (to be given later) is probably due to incomplete removal of water and shrinkage of the porous glass in the bakeout operation.

The foregoing results were obtained on early samples of porous glass. The surface area of the regular porous glass now being produced more probably is slightly above 200 sq.m. per gm. and the average pore radius is 20 a.u. Far from sufficient work, however, has been done to fix these as standard values, but they are given here to show the order of magnitude.

The shrinkage of porous glass has been determined at elevated temperatures. Measured 2-in. rods were placed in a cold furnace, heated to the desired temperature, removed after various intervals of time, cooled, and remeasured. Measurements were made with vernier calipers with an accuracy of 0.1 mm. Results at 700°, 800°, and 900°C. are given in Fig. 2. The time periods to bring the furnace to temperature were 4, 5, and $2^1/_2$ hours, respectively. The curves are seen to have a tendency to level off at each temperature to definite values.

The flow of liquids at 35°C. through 1.25-in. porous glass disks has also been measured at various pressure heads. This was done by observing the change in level of the liquid in a 0.2-ml. pipette that was attached to a metal part in which the disk was held in an annular clamping device, using thin rubber gaskets to make the seal. The disk had a free area of 4.9 sq. cm. and was submerged in the liquid in a beaker to eliminate any surface-tension effects. The flow was found to be directly proportional to the applied pressure and approximately inversely proportional to the thickness of the disks and the viscosity of the liquid. The results for water and acetone are given in Fig. 3.

(3) Process Completed—Firing Step

When the porous glass is heated to about 1200°C., complete consolidation of its structure takes place and the article shrinks to 65% of its original volume, equivalent to a linear shrinkage of about 14%. Under proper control, this shrinkage takes place with practically no change in shape. The gases within the pores are forced out and the glass becomes perfectly clear.

The final glass contains approximately 96% SiO_2, 3% B_2O_3, 0.4% $R_2O_3 + RO_2$ (chiefly Al_2O_3), and traces of Na_2O and As_2O_3. To melt directly, a clear glass of this composition would require special technique involving extremely high temperatures and even then the number of shapes into which it could be formed, particularly pressed shapes, would be very limited. The leaching process makes these extreme temperatures unnecessary, allows the use of regular glass batch materials, and makes possible the fabrication of a large variety of shapes which could not be made from such a high-melting glass in any other practicable way.

(4) Multiform Process

The leaching process, as mentioned earlier, is limited to relatively thin ware. For the manufacture of massive ware or of shapes that cannot readily be made by ordinary glassworking technique, the Multiform process can be used with the high-silica glass which has been made as described previously. This process consists essentially of pulverizing the glass, forming

[2] P. H. Emmett and T. W. DeWitt, "Low-Temperature Adsorption of Nitrogen, Oxygen, Argon, Hydrogen, *n*-Butane, and Carbon Dioxide on Porous Glass and on Partially Dehydrated Chabazite," *Jour. Amer. Chem. Soc.*, **65** [7] 1253–62 (1943).

[3] S. Brunauer, P. H. Emmett, and E. Teller, "Adsorption of Gases in Multimolecular Layers," *ibid.*, **60** [2] 309–19 (1938).

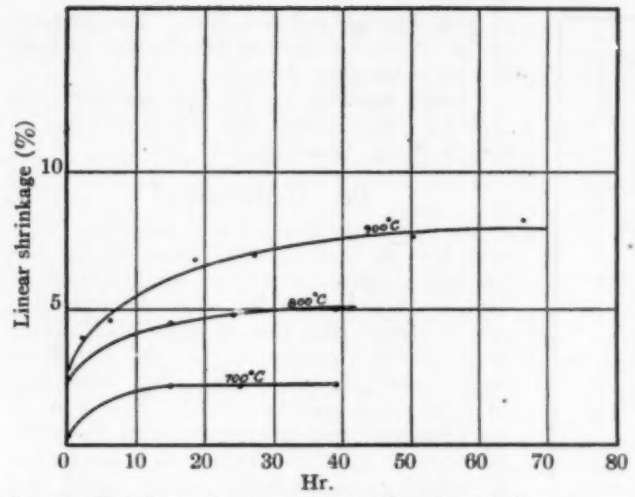

FIG. 2.—Shrinkage of porous glass as function of time at various temperatures; maximum possible shrinkage 14%.

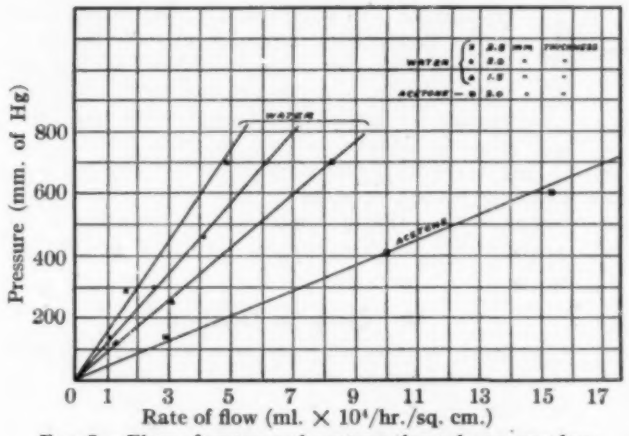

FIG. 3.—Flow of water and acetone through porous glass.

it by methods simulating ceramic techniques, and refiring. The resultant product is translucent or opaque white rather than transparent, but other properties in general are the same as those of the original high-silica glass.

III. Properties of Vycor-Brand Glasses and Comparisons with Other Brands

(1) Physical Properties

Physical properties of Vycor-brand glasses, No. 790 and Multiform No. 790 are compared with those of Pyrex-brand glass No. 774 and fused silica in Table I.

(*A*) *Density:* The density was measured at room temperature (24° to 27°C.) by the water-displacement method.

(*B*) *Expansion Coefficient:* The expansion coefficient, 7.5×10^{-7} per °C., in Table I is the average value for the range 0° to 300°C. as measured by the usual dial method. It is only one fourth the value for Pyrex-brand glass No. 774, which has the lowest coefficient of any glass now melted on a large scale, and is but slightly higher than that for fused silica. As a result of this low coefficient, No. 790 glass articles can be repeatedly heated to redness and plunged into water without breakage.

The expansion coefficient for Multiform No. 790 glass is about one point higher than for the clear form.

Saunders[4] has studied the expansion of No. 790 glass as a function of temperature. For his measurements, he used a modified interferometer in which he observed the differential between the sample and fused silica. Lillie[5] later used an evacuated interferometer, giving absolute measurements of changes in length. The expansion curves for 96% silica glass and fused silica as obtained by him are given in Fig. 4. It will be noticed that in the range of 500° to 700°C. the expansivity, as determined by the slope of the curve, is practically equal to that of the silica. It shows the usual rise as the temperature approaches the annealing point.

(*C*) *Viscosity:* Softening points were measured by the fiber method.[6] A special furnace was built for this purpose in which a platinum tube served both as the core and also as the resistor heating element. The temperature distribution in the furnace was adjusted at about 1500° to give the same effective length as a regular softening-point furnace at a lower temperature. Annealing-point measurements were made in the same furnace, with due consideration for

[4] J. B. Saunders, "Expansivity of a Vycor-Brand Glass," *Jour. Research Nat. Bur. Standards*, **28** [1] 51–55 (1942); R.P. 1445; *Ceram. Abs.*, **21** [4] 79 (1942).

[5] H. R. Lillie, "Expansion Characteristics of Corning 96% Silica Glass No. 790." Presented at the Forty-Fourth Annual Meeting, The American Ceramic Society, April 21, 1942, Cincinnati, Ohio (not published).

[6] H. R. Lillie, "Viscosity of Glass Between Strain Point and Melting Temperature," *Jour. Amer. Ceram. Soc.*, **14** [7] 502–11 (1931).

TABLE I

PHYSICAL PROPERTIES OF VYCOR-BRAND GLASSES

Property	Vycor-brand glass No. 790	Vycor-brand glass No. 790 Multiform	Pyrex-brand glass No. 774	Fused SiO_2
Density (gm./cc.)	2.18	2.15	2.23	2.20
Linear expansion coeff. (per °C. × 10^7)	7.5	8.5	33	5.5
Softening point (°C.)	1500		819	1650
Annealing point (°C.)	900		553	1150
Electrical resistivity (ohms-cm.)				
Log *R* at 250°C.	9.7	9.7	8.1	12*
Log *R* at 350°C.	8.1	8.1	6.7	9.7*
Dielectric constant (20°C.)	3.8	4.0	4.7	3.8
Refractive index (n_D)	1.458		1.474	1.458

* M. D. Rigterink, "Improved Ceramic Dielectric Materials," *Rev. Sci. Instruments*, **12** [11] 527–34 (1941); *Ceram. Abs.*, **22** [2] 33 (1943).

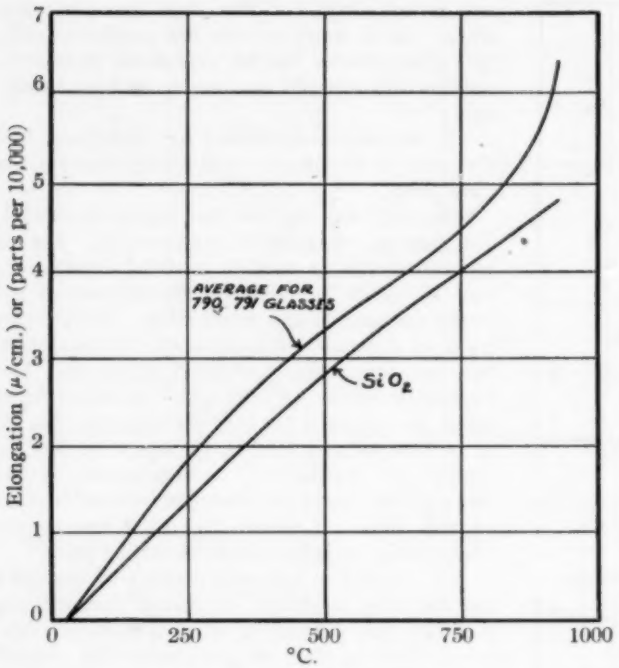

FIG. 4.—Expansion curves.

the effective furnace length, which was shorter than that of the regular annealing-point furnaces. Because the high-temperature measurements were difficult and only a few tests were made, only approximate values can be given. These are sufficiently precise, however, to show that the softening point of No. 790 glass is very high, approximately 700°C. above that of Pyrex-brand glass No. 774 and 150°C. below that of fused silica. The annealing point is approximately 350°C. above that for No. 774 and about 250°C. below fused silica.

(*D*) *Electrical Properties:* The volume resistivities of clear and Multiform No. 790 glasses are relatively high when compared with glasses in general although they are lower than that of fused silica. They are substantially equal for the two types of glass. The exact agreement shown in Table I may be fortuitous. The values given for the clear glass were obtained on samples as they came from the process. Resistivities of samples prepared by lampworking at high temperatures in an oxygas flame have been observed to average about three-fold higher at 250°C. and $2^1/_2$-fold higher at 350°C.

The power factor of No. 790 glass is very low, as would be expected from its composition. Samples have been measured with values well below 0.05% at 20°C. and at a frequency of one megacycle. The dielectric constants given in Table I were measured under the same conditions.

(*E*) *Mechanical Properties:* Because results of strength measurements vary considerably with the size, shape, and surface of the samples and with the testing conditions, an idea of the mechanical strength of No. 790 glass can perhaps best be given by stating that it is the same as that for a normally melted glass such as Pyrex-brand No. 774. The strength of the Multiform glass is substantially as high as that of the clear glass.

Young's modulus is also approximately the same for both the clear and Multiform types as for the Pyrex- brand glass.

IV. Devitrification

The rate of devitrification of glass No. 790 is very low at temperatures below 900°C. but becomes appreciable in the neighborhood of 1000°C. Up to 1200°C., this devitrification rate is greater than that of fused silica, owing to the lower viscosity of the No. 790 glass. Above 1200°, it falls progressively below that of fused silica, and at no point does it reach the relatively rapid rates observed for the latter in the range 1300° to 1500°C. It is accelerated by reducing gases, alkalis, alkaline earths, and certain other metallic oxides.

Just as in the case of fused silica,[7] devitrification takes place with the formation of cristobalite. It starts only at the surface and works slowly back into the body of the glass. Starting with a clear sample of No. 790 glass, no visible change is apparent even after prolonged heating at devitrifying temperatures until the glass is allowed to cool to below 300°C. On cooling below this temperature, the surface becomes suddenly frosted or etched. This effect is due to a surface crazing that accompanies the inversion β- to α-cristobalite which occurs in the range of 200° to 275°C.*

V. Chemical Durability

As would be expected from the nature of the process by which it is made wherein soluble constituents are removed, No. 790 glass is extremely stable toward all acids except hydrofluoric. Even in this acid, it is attacked considerably more slowly than are the conventional glasses. The rate in cold 60% hydrofluoric acid is only about one fifth as great as for Pyrex-brand glass No. 774 and still less when compared with lime glasses. It is also very stable toward water and all other neutral or acid solutions. Its durability is less in alkaline solutions, but even in such solutions it is generally superior to conventional chemical-resistant glasses. The rate of this solution is small at ordinary temperatures, and for most purposes it can be considered negligible. In this connection, it can be pointed out that because the glass contains only traces of elements other than silicon, boron, oxygen, and aluminum, the contamination of solutions in contact with the glass by any other substances, notably alkalis, will be extremely small. For this reason, the glass is particularly well adapted to certain high-precision analytical work. An example of this is its use in glass-durability measure-

[7] R. B. Sosman, Properties of Silica, p. 97. Amer. Chem. Soc. Monograph Series, No. 37; Chemical Catalog Co., Inc., New York, 1927; 856 pp. *Ceram. Abs.*, **7** [7] 505–506 (1928).

* See p. 131 of footnote 7.

ments that involve the determination of alkali released by the sample.

The losses in weight as the result of attack by three reagents at 100°C. are given in Table II.

Sections of tubing with fire-polished ends and with an area of 40 to 50 sq. cm. were used as samples. For the acid tests where the losses were extremely small, the weighings were made on a microbalance using tares and ultraviolet light to dispel electrostatic charges.[8] Results on four samples of No. 790 glass and also those on six samples of No. 774 agreed to within ±0.0002 mg. per sq. cm. They would undoubtedly vary with the nature of the surface, but they serve to show the low order of magnitude of the attack. The difference between the two glasses is in line with those found by Wickers, Finn, and Clabaugh[9] in normal sulfuric and six-normal hydrochloric acid. The alkali tests were made in the conventional manner using a regular analytical balance. Results so obtained agree to within about 10%.

The high softening point of No. 790 glass has extended its usefulness to higher temperatures than are possible with any other glass except fused silica. At these elevated temperatures, the glass is relatively inert to acid and neutral salts and refractory oxides, but it reacts with alkalis and alkaline salts or compounds which will decompose to form them. Electropositive metals, such as aluminum and magnesium in the molten state, also attack the glass. As the temperature increases, other substances, particularly basic oxides, become reactive, and this factor must be considered for certain applications. In spite of these limitations, No. 790 glass has been found very useful in many ashing, ignition, and calcining operations and is regularly employed at temperatures up to 1000°C.

The glass is inert toward chlorine and acid gases, such as HCl and SO_2 at all temperatures. Metals, such as lead and copper, whose oxides tend to flux with silica at high temperatures have no effect when heated in vacuum. In 2-hour tests in vacuum at 1150°C., no reaction was found with chromium, nickel, and all metals below the latter in the electromotive series.

VI. Maximum Operating Temperature

Since the applications of 96% silica glass are so varied in nature, it is difficult to state any definite maximum operating temperature. From the standpoint of deformation, the annealing point, 900°C., could probably be used as the highest temperature for continuous service. However, in view of the relatively low temperature coefficient of viscosity as shown by the wide spread between the annealing and softening points, considerably higher temperatures can often be tolerated. Shallow dishes and well-supported combustion tubes of No. 790 glass in fact have frequently been found useful in the laboratory at temperatures up to 1200°C.

[8] C. J. Rodden, "Removal of Static Charges from Glassware by Ultraviolet Light," *Ind. Eng. Chem., Anal. Ed.*, **12** [11] 693 (1940).

[9] Edward Wichers, A. N. Finn, and W. S. Clabaugh, "Comparative Tests of Chemical Glassware," *Jour. Research Nat. Bur. Standards*, **26** [6] 537–56 (1941); RP 1394; *Ceram. Abs.*, **20** [9] 214 (1941).

TABLE II

CHEMICAL DURABILITY OF VYCOR- AND PYREX-BRAND GLASSES

	Vycor-brand glass No. 790 (mg./sq. cm.)	Pyrex-brand glass No. 774 (mg./sq. cm.)
5% HCl (24 hr.)	0.0005	0.0045
$N/50$ Na_2CO_3 (6 hr.)	0.07	0.12
5% NaOH (6 hr.)	0.90	1.4

From the standpoint of devitrification, 900°C. is again an approximate limit for long continuous service provided the glass is clean and not in contact with materials which react with the glass. For shorter operations, particularly where it is not essential that the glass remains clear, higher temperatures are possible. In some applications, it is possible to increase service life at these higher temperatures by not allowing it to cool below 300°C. and thus avoid checking or spalling as a result of the β- to α-cristobalite inversion. It has been found that devitrification may actually reduce deformation under these conditions.

To determine constancy of weight of No. 790 glass, 50-ml. crucibles were ignited at 800° to 850°C. in an electric muffle. Changes in weight after one hour of ignition were within the accuracy of weighing on the ordinary analytical balance.

VII. Lampworking Properties

One feature of the unique manufacturing process is that it is often possible to perform lampworking operations on the original relatively soft glass before converting to the high-silica form. For example, flanged or closed-end cylinders can advantageously be made in this way. For special apparatus, however, or for the production of larger ware than can be conveniently processed, such as long lengths of tubing, it is often desirable or necessary to lampwork the final high-silica or No. 790 glass.

The lampworking properties of the glass are similar to those of fused silica. A much higher temperature is necessary than that for ordinary glasses but not quite so high as for silica; in this respect, it is easier to work than the latter. For smaller items, an oxygas flame is satisfactory, but oxyhydrogen may be necessary for larger operations. Just as in the case of fused silica, No 790 glass does not flow as readily even at high temperatures as do ordinary glasses. On the other hand, the high heat-shock resistance makes it possible to heat the glass quickly or even to spotwork relatively large pieces without breakage. The temperature required for making seals is so high that silica volatilization occurs and the vapors condense on cooler portions around the seal to form a white bloom. This effect can be minimized by limiting the heating to as low a temperature as possible and the bloom, if not allowed to become too heavy, can usually be dispelled by heating or sometimes by treatment with dilute hydrofluoric acid.

Since the temperature at which the glass was fired to consolidate the porous structure is considerably lower than that required for lampworking, there may

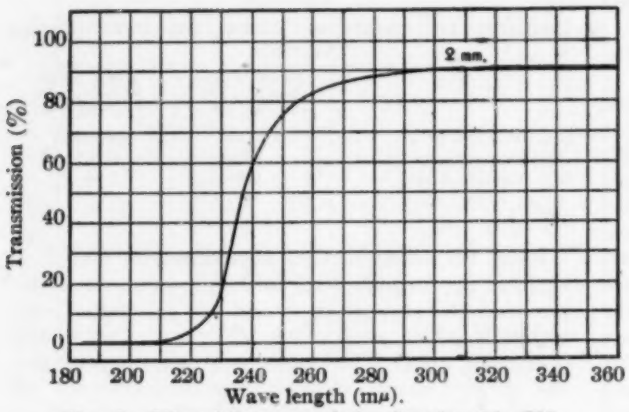

FIG. 5.—Ultraviolet transmission for glass No. 791.

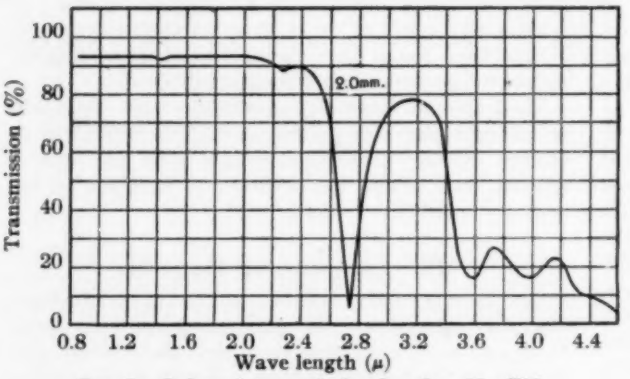

FIG. 6.—Infrared transmission for glass No. 790.

be a tendency to form bubbles in the latter operation. These bubbles are sometimes produced when seals are made in tubing, which is regularly furnished for such ware as combustion and thermocouple-protection tubes. They ordinarily do not impair the usefulness of the seal except in appearance and loss of clarity and can be kept at a minimum by working again at as low a temperature as possible.

Articles of Multiform No. 790 glass can be sealed together or to the clear No. 790 glass, and either form can be sealed directly to fused silica, although each requires a graded seal for joining to higher expansion glasses.

No alloy has yet been developed that matches the expansion characteristics (up to the setting temperature) of 96% silica glass. Invar[10] has an unusually low coefficient of expansion only at relatively low temperatures. It is, therefore, necessary in general to use graded seals or intermediate sealing glasses for introducing metal electrodes or other parts through envelopes for lamps or special tubes.

VIII. Optical Properties

Glass No. 790 is highly transparent to visible light. The ultraviolet transmission is usually very high at wave lengths longer than about 365 mμ. Below that wave length, it falls off and at 254 mμ may vary from practically 0 to 10% or more for a 2-mm. thickness.

Vycor-brand glass No. 791 is produced for purposes requiring high transmission at wave lengths down to 254 mμ or less. Aside from transparency to ultraviolet light, the properties in general are identical to those of glass No. 790. It is regularly tested at 254 mμ and is guaranteed to have a transmission at this wave length of 70% for a thickness of 2 mm., but the transmission is usually higher than this. It should be pointed out that all values given in this section are for observed transmission uncorrected for reflection losses. The maximum possible transmission for zero light absorption in the glass is about 92%. The average transmission curve obtained on six samples taken from four random lots of No. 791 glass is shown in Fig. 5. The maximum deviation for individual samples was 1% for wave lengths down to 254 mμ. Samples were polished plates of 2-mm. thickness.

The loss in transmission as a result of solarization is much less than for other commercially available ultraviolet-transmitting glasses except fused silica. In tests made from time to time by exposing polished plates under a 500-watt Hanovia quartz arc for 100 hours, the loss for a 2-mm. thickness at 254 mμ has averaged about 6% and has not exceeded 9% of the original value. Longer exposures have not increased this loss, indicating that the solarization was complete after 100 hours.

Its high transmission and low solarization make No. 791 a particularly useful glass for mercury-vapor and similar lamps intended for maximum production of ultraviolet light. The glass is ordinarily opaque to 185-mμ radiation and for that reason there would be no ozone generated around a lamp made with it. More recent developments, however, have shown that it is possible to prepare 96% silica glass with an appreciable transmission even to this short wave length if this is desired. The glass is also well suited for optical filters and windows when both high and constant transmission is desired.

The infrared transmission of No. 790 glass for a thickness of 2 mm. is given in Fig. 6. It is very high at wave lengths up to about 3.3 μ with a relatively sharp absorption at 2.75 μ. The infrared transmission of glass No. 791 is practically identical with that of No. 790 glass.

The refractive index, $n_D = 1.458$, is the same for both No. 790 glass and No. 791 glass.

IX. Summary

Vycor-brand glass No. 790 containing 96% silica is produced without the use of excessive melting temperatures by a process in which a relatively soft borosilicate glass is melted and shaped, the fluxes are removed by leaching, and the residual porous high-silica structure is consolidated by heating. The outstanding

[10] J. W. Sands, "Invar, Elinvar, and Related Iron-Nickel Alloys," *Metals & Alloys*, **3**, 131–35, 150 (1932).

properties of this glass are its very low coefficient of expansion and correspondingly high resistance to heat shock, its high softening point, low power factor, and high chemical durability, which make it useful for varied applications in the industrial and electrical fields as well as in the laboratory. The glass can be used continuously at temperatures up to 900°C. or for limited service at much higher temperatures provided it is not in contact with materials which react with or cause devitrification of silica. It can be lamp worked by methods similar to those used for fused silica.

Porous glass is formed as an intermediate product in the process. It is characterized by pores of very small and relatively uniform radius, the average of which is in the order of 20 a.u.

A translucent or opaque white glass is made by the Multiform process, which enables the production of massive ware and a variety of shapes that cannot be made directly in the clear form. Aside from transparency, the properties in general are the same as those of the clear glass.

Vycor-brand glass No. 791 is highly transparent to ultraviolet light at wave lengths down to 254 mμ or less, and glasses have been made with an appreciable transmission even at 185 mμ. Glasses No. 790 and No. 791 are highly transparent to the near infrared.

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ANALYSIS OF BATCH FOR SEGREGATION*

By H. J. Hunt

Abstract

Factors influencing the accuracy of tests for segregation in glass batches are discussed. Recommendations are given as to optimum sample size. Methods of correction for cullet in the samples taken for analysis and for comparison of the results with a standard miniature batch are described.

I. Introduction

It is generally considered that poor mixing of glass batch or segregation during handling can be a cause of cord and other glass defects. It is therefore sometimes necessary to examine into the state of mixing and to determine what degree of homogeneity exists in a glass batch.

The problem has been considered frequently in the past and the batch is usually sampled at the mixer, the conveyer, or the container, and partial or complete analysis is performed on such samples. The analysis of these samples can be compared with the correct value or with themselves to judge the degree of uniformity being achieved. Granular materials seem more likely to be distributed in a nonuniform manner than material of fine particle size.

There are various methods of examining batches for homogeneity. (1) A complete analysis can be made; (2) the material insoluble in hydrochloric acid can be determined; (3) for many lime glass batches, the determination of sodium oxide in water extract and of lime in a subsequent acid extract can be made; and (4) this company at times has determined china clay or barium carbonate in certain batches where lumping was suspected.

In the work of which this paper forms a part, segregation of soda ash and of borax could be noted in some cases on the top of the batch wagons. The larger particles of soda ash and borax rolled to the edge of the pile. It was desired to determine the quantitative effect of such segregation and also whether it extended throughout the batch mass.

It is not the purpose of the writer to give the actual analytical procedures because these are well covered in the literature,[1] but three important factors involved in the chemical investigation of batch inhomogeneity will be described. These are (1) size of sample, (2) effect of cullet, and (3) comparison with miniature batch.

II. Size of Sample

Tooley[2] has a conception which he calls the "unit of homogeneity." This is the smallest volume of batch in which the composition is the same as that desired; for example, if a 1-ton container of batch is divided into two parts, the same proportions of the ingredients determined might be found in each half. In that case, the the unit of homogeneity would be large, 1000 lb., and no good degree of homogeneity would be assured. If, however, the variation shown among a number of 1-lb. samples is small and they do not differ much from the standard analysis, some presumption of homogeneity can be made. If, moreover, 1-ounce samples exhibit a good degree of uniformity, a higher degree of homogeneity is established.

* Presented at the Autumn Meeting, Glass Division, The American Ceramic Society, September 15, 1943, Uniontown, Pa. Received February 29, 1944.

(1944)

[1] (*a*) W. W. Scott, Standard Methods of Chemical Analysis, Vol. II, p. 2253, 5th ed. D. Van Nostrand Co., Inc., New York, 1939.
(*b*) *Ibid.*, Vol. I, pp. 168–75.
(*c*) R. C. Griffin, Technical Methods of Analysis, pp. 29–32, 2d ed. McGraw-Hill Book Co., New York, 1927.
(*d*) W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, pp. 611–13. John Wiley & Sons, Inc., New York, 1929; *Ceram. Abs.*, **9** [1] 68; [10] 888 (1930).

[2] Personal communication of F. V. Tooley to J. F. Greene.

The necessary size of the unit of homogeneity depends on the self-mixing qualities of the batch during melting, on the furnace characteristics, and on the product to be made from the glass. Some products obviously can tolerate greater inhomogeneities than others. In the present work, the samples consisted of a tablespoon of mixed batch and cullet, about 20 to 30 gm.; after removal of cullet, the sample weight was between 10 and 15 gm.

III. Effect of Cullet

The typical glass batch consists of fresh batch or new batch plus cullet. If the cullet is regularly mixed with batch at the mixer, any tests for poor mixing or segregation should be made on such cullet-containing batch because the cullet may exert some effect on the mixing process. The scales used for weighing cullet are frequently less accurate than those used for other ingredients. The exact proportion of cullet may therefore vary in the batch. In small samples, a large lump of cullet may greatly affect the proportions of fresh batch to cullet. It is better, therefore, to calculate the results to the cullet-free basis.

If the amount of cullet present is small and the particles relatively large, it can be picked out by hand. The few fine particles that are missed will have little effect on the percentage of the desired ingredients. If the percentage of cullet used is high and if there is a large percentage of fines in the cullet, it is important to remove or account for all the cullet.

Table I shows the relative effect on the percentage of the desired constituent X resulting from varying amounts of cullet left in the sample after hand picking. In example (1), the amount of cullet is small compared to the total weight of batch and therefore if 10% of it is missed, the effect on the percentage of X is also small, in this case amounting only to 0.13%. If, however, the amount of cullet being used is as large as 50% of the total batch, the situation would be as shown in example (2). The effect on the percentage of constituent X in this case is much greater, amounting to 0.9%.

Complete removal of cullet by screening is not possible. The coarser particles can be removed, but cullet often contains a large percentage of particles similar in size to the batch ingredients.

Separation by density is not feasible because the densities of various cullets lie between those of various batch ingredients. It would be necessary to make at least two such separations to remove cullet from heavier and lighter batch materials. Various drying operations would be required, and a high degree of temperature control would be necessary to effect some of the separations.

It is possible to screen out the greater part of the cullet in one or more stages, and then from the known size distribution of the grains, that part which cannot be removed by screening can be calculated.

The determination of Na_2O and B_2O_3 was accomplished by the following steps: (1) Make screen analyses of cullet stock and all batch ingredients; (2) sample batch at as many points as may be desired; (3) remove coarse cullet by passing mix through the finest screen that will pass all batch materials; (4) weigh all fine materials, extract with hot water, and remove filtered aliquots for titration; (5) screen wet insoluble residue through sieve that will pass all insoluble batch constituents; (6) dry and weigh cullet retained by this second screen; and (7) calculate weight of cullet passing second screen from known size distribution of cullet.

A container of batch is sampled at the furnace and a number of single spoon samples are obtained at intervals during fillings. These are labelled to indicate place and time of sampling.

Each individual sample is passed through an 8-mesh screen to remove the coarse cullet and is weighed, W_1. The sample is then extracted with hot water to dissolve all soluble materials, some of which may be coarser than is permitted for the more refractory ingredients. The extract is made up to 250 cc. and an aliquot of 100 cc. is removed. The aliquot is filtered to remove very fine insoluble material and the clear filtrate is titrated[1] for Na_2O and B_2O_3.

TABLE I

ERROR DUE TO INCOMPLETE REMOVAL OF CULLET

	Example (1) (lb.)	Example (2) (lb.)
Fresh batch	2000	2000
Cullet	300	2000
Fine cullet (10%) missed	30	200
Ingredient X	200	200
	X (%) in fresh batch	
Actual	$\frac{200}{2000} \times 100 = 10\%$	$\frac{200}{2000} \times 100 = 10\%$
Apparent	$\frac{200}{2030} \times 100 = 9.87\%$	$\frac{200}{2200} \times 100 = 9.1\%$
Error	0.13%	0.9%

The wet insoluble residue from the water extract is next screened through a 35-mesh screen, which removes the cullet between 8- and 35-mesh; the other insolubles and fine cullet pass. The cullet on 35-mesh is washed, dried, and weighed, W_2. From the screen analysis of the cullet, the ratio (R) of all cullet passing 8-mesh to the cullet between 8- and 35-mesh is obtained. Thus the weight of all cullet passing 8-mesh can be calculated, $W_3 = R \times W_2$. Finally, the weight of fresh batch taken, W_4, can be obtained by subtracting W_3 from W_1. From this weight, W_4, it is possible to calculate the percentages of the ingredients determined on the basis of fresh batch alone.

An example of this method of calculation follows:

Batch wt. + cullet through 8-mesh = W_1 (10.000 gm.)
Cullet wt. retained on 35-mesh after wet sieving = W_2 (0.677 gm.)
Cullet wt. through 8-mesh = W_3 ($0.677 \times 1.22 = 0.826$)
Fresh batch taken (wt.) = $W_4 = W_1 - W_3$ (9.174 gm.)

The ratio, R, 1.22 in the foregoing example, was derived from an average of nine screen analyses on the

TABLE II

SCREEN TESTS ON CULLET TO ESTABLISH RATIO (R)

Sample No.	Retained on 8-mesh (%)	Retained on 35-mesh (%)	Through 35-mesh (%)	Ratio $\frac{(2)+(3)}{(2)} = (4)$
	(1)	(2)	(3)	(4)
1	84.9	11.9	3.2	1.27
2	85.2	10.9	3.9	1.35
3	88.1	9.6	2.3	1.24
4	81.6	14.7	3.7	1.25
5	84.3	12.4	3.3	1.27
6	85.6	12.2	2.2	1.18
7	79.6	17.8	2.6	1.17
8	82.7	15.0	2.3	1.16
9	89.0	9.0	2.0	1.22
Avg.	84.6	12.6	2.8	1.22

particular cullet, and the results of these analyses are given in Table II. The method of calculating R from this average is as follows:

	(%)
Cullet retained on 8-mesh	84.6
Through 8-mesh on 35-mesh	12.6
Through 35-mesh	2.8
	100.0

$$R = \frac{12.6 + 2.8}{12.6} = 1.22$$

This method of removing or accounting for cullet may be used even though the proportion of cullet in the batch varies. Some degree of constancy, however, is necessary in the particle-size distribution of the cullet. In the foregoing example, it is necessary that the ratio of cullet passing 8-mesh to the cullet between 8- and 35-mesh be of such constancy that variation in the ratio does not seriously impair the results. For example, in Table II, the maximum variation from the average of this ratio is 0.13; this would affect the percentage of ingredients sought in the case of mix B, Table III as shown in formula (1).

$$\frac{(\Delta R \times W_2)}{W_4} \%X = \Delta\%X \qquad (1)$$

$$\frac{0.13 \times 0.677}{9.174} \times 6.75 = 0.06\% \ Na_2O.$$

$$\frac{0.13 \times 0.677}{9.174} \times 7.99 = 0.08\% \ B_2O_3.$$

Since the average value of 1.22 for R is used in accounting for the cullet, it follows that in the previous example the possible error in the determination of Na_2O or B_2O_3, owing to uncertainty from this cause, is in the order of $\pm 0.07\%$. With batches containing a larger percentage of finely ground cullet, the uncertainty would be greater or with smaller amounts and coarser grinding it would be less.

Experiments in this laboratory have shown that the ratio, R, as determined on cullet alone, holds good even though the cullet is later mixed into the batch. To test this point, a sufficient number of screen analyses were made on the cullet stock to establish a ratio, R. A special batch was then mixed containing this cullet together with the same weight of fresh batch normally used in the mixer. In this batch, however, water-soluble materials of approximately the same grain sizes were substituted for those which in practice would be insoluble. Ten small samples taken from this batch were then treated as outlined, except that the cullet passing 35-mesh was determined as well as the cullet retained on this screen. In this way, it was possible to compare the actual weights of cullet in these samples with those calculated by use of the ratio previously determined. The variations so found could not in any case cause errors in the percentages of the constituents determined greater than those in the example cited.

TABLE III

TEST RESULTS ON TWO MIXES OF DIFFERENT DEGREES OF HOMOGENEITY

Sample No.	Na_2O (%)	Deviation from avg.	B_2O_3 (%)	Deviation from avg.
	Mix A			
1	6.67	0.05	7.89	0.07
2	6.55	.17	7.76	.20
3	7.08	.36	8.48	.52
4	6.49	.23	7.56	.40
5	6.82	.10	8.11	.25
Avg.	6.72		7.96	
Spread (max.-min.)		0.59		0.92
	Mix B			
1	6.71	0.04	7.92	0.07
2	6.74	.01	7.95	.04
3	6.70	.05	7.91	.08
4	6.79	.04	7.99	.00
5	6.82	.07	8.17	.18
Avg.	6.75		7.99	
		(%)		(%)
Spread (max.-min.)		0.12		0.26
Calculated value (from batch formula)		6.95		8.10
Analysis of standard sample		6.90		8.03

IV. Comparison with Miniature Batch

In some glass batches, reactions take place between certain ingredients during water extraction. These reactions must be allowed to go to completion by using successive extracts or by permitting adequate time. It may be necessary to add various reagents at this stage in order to remove from solution ingredients which would interfere with the subsequent analysis. The chemist has wide latitude at this point in handling batches of varied compositions.

To evaluate the results obtained by analysis, they can be compared with the composition calculated from the known batch formula. This calculation, however, may be of doubtful value in the case of some complex mixtures. In such cases, it is preferable to determine the standard values by actual analysis of a miniature batch. For this purpose a sample of approximately 10 gm. total is prepared by mixing all ingredients except cullet, each ingredient being accurately weighed according to the batch formula. The entire miniature batch is extracted and analyzed by the same procedure as used for actual samples. The resulting figures constitute the "standard analysis" of the batch. They are the percentages that would be obtained in

actual samples if no errors in mixing or segregation occurred. Even though a number of small samples from a given batch are uniform among themselves, there is something amiss in the process of batch preparation if they differ from this standard.

V. Examples

Table III shows the results obtained by analyzing two variant forms of a borosilicate batch. The two mixtures contain the same percentages of oxides but differ slightly in the ingredients used. The purpose of the analysis was to determine which batch would show less segregation under actual operating conditions. Sodium oxide and boric oxide were determined by titration and the percentages were calculated to the cullet-free basis, sample weights being corrected for cullet by the method described. In both mixes, there were 3600 lb. of cullet per ton of sand. The screen analysis of this cullet is shown in Table II.

The degree of homogeneity can be judged either from deviation of the individual samples from the average or from the spread between the high and low figures. By either criterion, it is evident that mix B shows greater uniformity throughout than mix A.

VI. Conclusions

It has been shown that by using small samples, removing or accounting for the cullet, and standardizing the method on a miniature batch, valuable information can be obtained as to the homogeneity of batch mixture.

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SIGNIFICANCE OF TOPOCHEMICAL FACTORS ON RATE OF REACTIONS BETWEEN SOLID SALTS*

BY GUNTHER COHN†

ABSTRACT

The factors determining the rate of reactions between solids are discussed. When the solid phases are internally in equilibrium and when equilibrium also is established at the phase boundaries, the kinetics are given by the geometric dimensions of the system, the free energy decrease, and the mobility of the diffusing particles in the reaction product. These conditions are not fulfilled in most practical cases, the reactions being strongly dependent on topochemical factors. Topochemical imperfections in crystals and their influence on the reaction velocity are described, but the mechanism of reactions influenced by topochemical factors can only be found empirically. The way of approach is outlined for the case of spinel formation from zinc oxide and iron oxide.

I. Introduction

Reactions in the solid state may be defined as chemical processes in which one or more solid reaction products are formed under diffusion of elementary particles through their interior. The layer of reaction products increases by chemical reaction with the phases adjacent to its boundaries. These adjacent phases may be in any state of aggregation, but in the present paper only reactions between entirely solid phases are discussed. Chemical changes of solids which do not involve a penetration of particles through solid phases are by definition not reactions in the solid state.

Solids in contact with each other may react additively as $A + B \rightarrow AB$ or in form of exchange reactions such as $AB + CD \rightarrow AC + BD$ or $AXO_n + BO \rightarrow BXO_n + AO$. All reactions in the solid state are composed of one or several steps of additive or exchange reactions. The reaction products are formed between the reacting phases. The number of new phases which appear in the course of a reaction in the solid state is given by the following factors: (*a*) the composition of the reaction products, (*b*) the sequence in which they are formed, (*c*) the miscibility with the parent phases, and (*d*) the nature of the particles by the motion of which the reaction is accomplished. In recent times, a host of reactions in the solid state have been studied in detail.[1,2] The photomicrograph shown in Fig. 1 represents the reaction[3] $ZnO + Al_2O_3 \rightarrow Al_2ZnO_4$; the spinel has completely surrounded the original alumina crystals and therefore must have grown by diffusion.

II. Rate-Determining Factors

The kinetics of reactions in the solid state are usually very involved because the reacting systems are heterogeneous and because the concentration of reacting particles in the diffusion layer is not only a function of time but also of space. In the solid state, an equaliza-

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† This study was carried on at the School of Chemistry, University of Minnesota; the author is now associated with Baker & Company, Newark, N. J.

[1] (*a*) J. A. Hedvall, Reaktionsfähigkeit fester Stoffe. J. A. Barth, Leipzig, 1938. 243 pp.; *Ceram. Abs.*, **17** [4] 164 (1938).

(*b*) J. A. Hedvall and Gunther Cohn, "Reactions in Solid State," *Kolloid-Z.*, **88** [2] 224–40 (1939); *Ceram. Abs.*, **19** [8] 203 (1940).

[2] W. Jost, Diffusion und chemische Reaktion in Festen Stoffen. Theodor Steinkopff, Leipzig, 1937; *Ceram. Abs.*, **17** [8] 292 (1938).

[3] K. Hild, "Formation of Spinel Al_2ZnO_4 by Reaction in Solid State," *Z. Phys. Chem.*, **A161** [4–5] 305–14 (1932); *Ceram. Abs.*, **12** [1] 36 (1933).

tion of concentrations by convection is not possible so that the diffusion of reacting particles is inherent in the mechanism and may even become dominant. The rate-determining factors can be summarized as follows: (1) the spatial and temporal sequence in which all possible phases appear, (2) the reactions at the phase boundaries, and (3) the diffusion in the interior of the solid phases. The phase-boundary reactions involve the following processes: (*a*) the transfer of matter from one phase to the other, (*b*) chemical reactions, and (*c*) formation of nuclei and growth of the reaction products.

Owing to this complexity, only a few reactions in the solid state have thus far been explained in detail. In nonregular crystals, moreover, the velocity of the different steps is dependent on the crystallographic direction. In powder mixtures, which are usually employed in studying reactions in the solid state, the directional effects may be neglected and average values may be assumed.

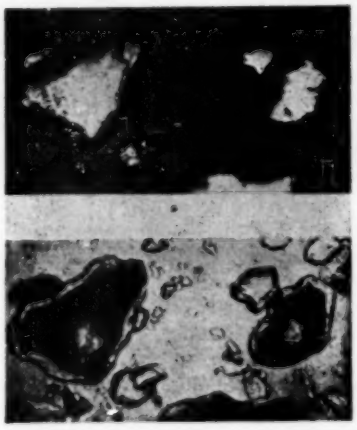

FIG. 1.—Formation of zinc-aluminum-spinel (from Hild[3]).

To bring out the kinetic conditions of a reaction, it is useful to consider the chemical potential of the diffusing particles in the different phases. A simple example is the reaction, $A_{solid} + B_{solid} \rightarrow AB_{solid}$, assuming that only one phase, AB, can exist which is not miscible with A or B. If, furthermore, only the A particles are able to diffuse, two different cases are possible, shown schematically by Fig. 2, in which the chemical potential of A is plotted as a function of the distance in the system. In phase A, the chemical potential of the A particles is constant. The A particles enter the reaction product AB at phase boundary I and diffuse through it toward phase boundary II under continuous decrease of the chemical potential. At phase boundary II, the A particles disappear by reaction with B and the chemical potential of A becomes zero behind phase boundary II.

In case I, the phase-boundary processes are much faster than the diffusion in the interior of AB. Under these conditions, equilibrium is permanently maintained at the phase boundaries in the course of the reaction and the diffusion in AB is alone rate determining.

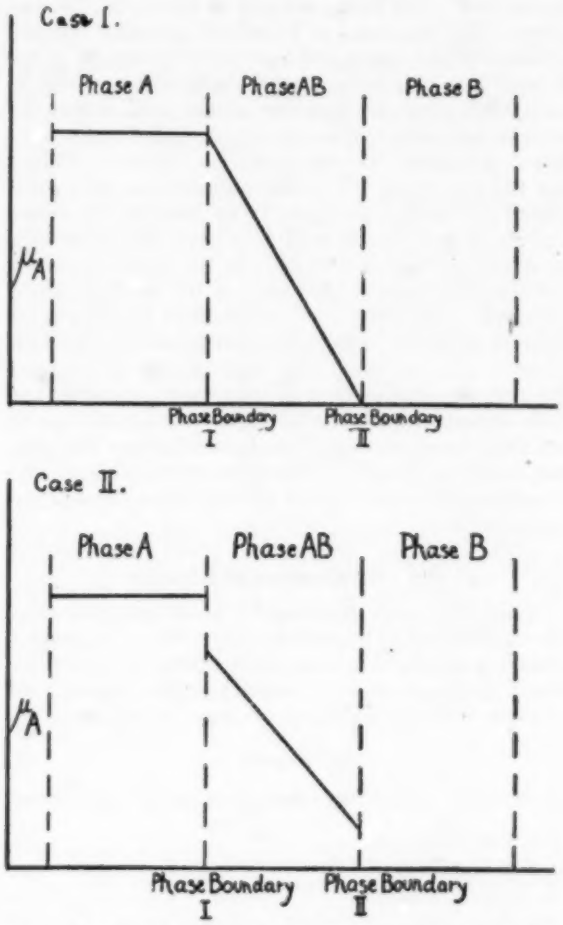

FIG. 2.—Chemical potential of diffusing particles during reaction.

In case II, the phase-boundary reactions are not infinitely rapid compared with the diffusion velocity. Because the transition of A particles from phase A to phase AB at phase boundary I requires time and likewise the chemical reaction between A and B at phase boundary II, equilibrium is not established at the phase boundaries. The diffusing substance is accumulated at phase boundary II. The gradient of the chemical potential under conditions otherwise equal is smaller than in case I and the reaction is slowed down. With increasing growth of the layer of AB, the influence of the diffusion on the rate increases so that finally case II might change to case I.

Case I is simpler than case II because all phase-boundary processes can be neglected. Figure 2, however, shows that, in very thin diffusion layers or in case of a very rapid diffusion, the phase-boundary processes may become predominant and may be studied.

The kinetic laws of reactions in the solid state can be deduced only from observed rates when the following conditions are fulfilled: (1) the phases involved in the diffusion must be internally in equilibrium and (2) equilibrium must also be maintained at the phase

boundaries. The first condition is due to the circumstance that the rate is primarily governed by the gradient of the chemical potential of the reacting particles. It is only defined when the particles present in each single phase are arranged in such fashion that the state of minimum free energy is maintained within each phase throughout the course of the reaction. This is not the case when the partaking solids are of a topochemically faulty structure. The rate then becomes undefined and is influenced to a large extent by incidental or external conditions. In this instance, only a qualitative picture of the course of the reaction can be obtained. The latter case is frequent and of great practical importance. The second condition is required for a kinetic analysis because the state of solid surfaces and the contacts between them are likewise little defined and little reproducible. Despite their great significance in reactions between solids, the phase-boundary processes can hardly be brought under controlled conditions, and a quantitative treatment of the reactions, therefore, is not possible.

III. Application of Kinetics

When the kinetic treatment is possible, the reaction rate is obtained by considering the diffusion velocity of those particles which move through the reaction products. In case of an additive reaction, A + B → C, the reaction rate is approximately given by equation (1).

$$dn/dt = kA/x \tag{1}$$

dn/dt = flow of reacting particles (moles or equivalents/sec.).
k = rate constant.
A = cross section of diffusion layer.
x = thickness of diffusion layer.

This relation has been found to hold in a few instances. In the rate constant are contained the kind and the concentration of diffusing particles and the gradients of their chemical potential. Explicit expression for the rate constant can be obtained in the following way. The diffusing particles which enter into the layer of reaction products are at the same time constituents of the reaction products. The composition of the reaction products, therefore, must always vary and deviate from the stoichiometric product. For each kind of constituent, the deviations from the stoichiometric composition are greatest at the phase boundary at which the particles enter the diffusion layer and decrease toward the opposite phase boundary. The rate constant is found by calculating the speed with which the local deviations from the stoichiometric composition of a crystal are removed by self-diffusion. Because fresh reacting particles enter the diffusion layer at the phase boundaries, the deviations from the stoichiometric composition are permanently generated during the reaction. This holds even when the solubility of the components in the reaction products is so small that the phases are classified as immiscible because minute deviations from the stoichiometric composition might be sufficient to maintain the diffusion and the progress of the reaction.

Rate constants may be calculated for all types of reactions. The calculations, at the present time, however, can be verified only experimentally on reactions between ionic crystals in which the self-diffusion coefficients are derived from the electrolytic conductivities. Self-diffusion coefficients have not yet been determined directly in inorganic substances. As an example, the resulting rate constant is given for reaction (2), which has been calculated by Wagner.[4]

It is assumed that the reaction is performed by a motion of A and B particles having charges of equal sign and moving from opposite phase boundaries through the layer of reaction product.

An integration of equation (3) is not possible, inasmuch as the dependence of the partial conductivities (product of transference number and total conductivity) and of the particle concentrations on the chemical potential of AX_m in the diffusion layer cannot be estab-

[4] Carl Wagner, "Mechanism of Formation of Ionic Compounds of High Order (Double Salts, Spinels, Silicates)," *Z. Phys. Chem.*, **B34**, 309 (1936).

$$AX_m + BX_n \rightarrow ABX_{m+n} \tag{2}$$

$$k = \frac{300}{96{,}500}\ \frac{1}{Ne} \int_{\mu_{AX_m} \text{ at phase boundary } ABX_{m+n}/BX_n}^{\mu_{AX_m} \text{ at phase boundary } AX_m/ABX_{m+n}} \frac{t_A t_B}{t_A + t_B} \times \kappa\ \frac{c_A + c_B}{c_B}\, d\mu_{AX_m} \tag{3}$$

c_A = concentration of A in ABX_{m+n} (equiv./cm.³)
c_B = concentration of B in ABX_{m+n} (equiv./cm.³)
κ = total conductivity of ABX_{m+n}
t_A = transference number of A in ABX_{m+n}
t_B = transference number of B in ABX_{m+n}
μ_{AX_m} = chemical potential of AX_m (per equivalent)
N = Avogadro's number
e = electronic charge

$$k = \frac{300}{96{,}500}\ \frac{1}{Ne}\ \frac{\bar{t}_A \bar{t}_B}{\bar{t}_A + \bar{t}_B}\ \bar{\kappa}\ \frac{\bar{c}_A + \bar{c}}{\bar{c}_B} \left[\mu_{AX_m \text{ at } AX_m/ABX_{m+n}} - \mu_{AX_m \text{ at } ABX_{m+n}/BX_n} \right] \tag{4}$$

$$k = \frac{\bar{t}_A \bar{t}_B}{\bar{t}_A + \bar{t}_B}\ \frac{\bar{\kappa}}{96{,}500}\ \frac{\bar{c}_A + \bar{c}_B}{\bar{c}_B} E \tag{5}$$

TABLE I

EXPANDED LATTICE OF FRESH REACTION PRODUCT*

Ca_2SiO_4	Reflection angles of powder photographs $\theta/2$						
Normal lattice	15.10	16.50	17.50	21.00	26.30	28.50	31.60
Distorted lattice	14.90	16.40	17.40	20.90	26.10	28.40	21.40

* From Jander (see footnote 8, p. 312).

lished quantitatively. It is noteworthy, however, that an approximate integration has been possible in the corresponding rate expression of certain tarnishing reactions[5] on the basis of thermodynamic considerations of Schottky and Wagner[6] about the state of real crystals. In case of a reaction between entirely solid phases, average values of the partial conductivities and concentrations have to be taken in order to evaluate the integral as shown in equation (4).

This relation is most conveniently applied when the decrease of the chemical potential between the boundaries of the diffusion layer is measured as the electromotive force **E** of a suitable galvanic chain as shown in equation (5).

The reaction velocity is calculated from the geometric dimensions of the system and from (1) the change in free energy involved in the reaction and (2) the mobility of the building stones of the reaction product. In principle, therefore, the kinetics of this group of reactions in the solid state are completely understood. In the instance of the reaction, $2AgI + HgI_2 \rightarrow Ag_2HgI_4$, excellent agreement was found between the calculated and observed reaction rates.[7] The reaction mechanism is represented schematically in Fig. 3. The reaction is performed by silver ions and mercuric ions moving through the layer of Ag_2HgI_4 and reacting at the respective opposite phase boundaries. The observed rate constant at 65°C. was 2.1×10^{-11} equivalent cm.$^{-1}$ sec.$^{-1}$, the calculated was 1.9×10^{-11} equivalent cm.$^{-1}$ sec.$^{-1}$. Among the few reactions investigated, however, this is the only instance in which the theory could be confirmed, obviously only because of the anomalously disordered state of the high-temperature modification of Ag_2HgI_4. The reason for the failure of the theory in other tests was that the components involved were internally not in equilibrium or (and) that equilibrium was not established at the phase boundaries.

IV. Influence of Topochemical Factors on Reaction Rate

In solid-phase reactions, it is always possible that the reaction products are not formed in the thermodynamically stable state but as imperfect and abnormally energy-rich (active) intermediates. The imperfections can occur (*a*) as an unstable modification, (*b*) as an expanded or deformed lattice, (*c*) as holes and cracks of atomic dimensions, (*d*) as an irregular displacement of lattice particles, (*e*) as colloidal dimensions, or (*f*) as the amorphous state. Despite their thermodynamic instability, the intermediate states may have a long lifetime, sometimes indefinitely long, because the particle motion necessary for a rearrangement is strongly hindered in the solid state and requires considerable activation energies. The unstable states appear also at temperatures at which the reversible lattice disorder[8] should be established. The presence of the excess of one or more constituents in the reaction product may further increase and also stabilize the lattice imperfection.

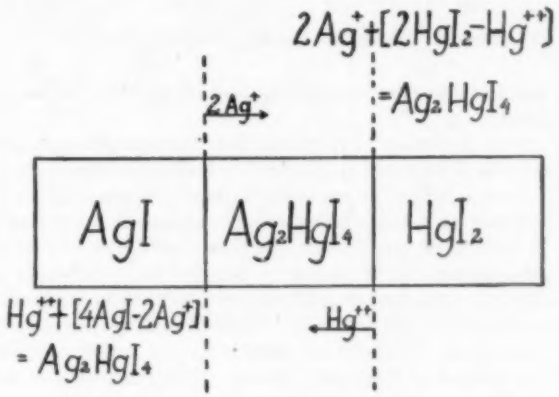

FIG. 3.—Mechanism of formation of Ag_2HgI_4 (from Koch and Wagner[7]).

These imperfections are different from the reversible, thermodynamically required disorder.[8] They may not be obtained from equilibrium states because they need not represent an equilibrium state at any temperature.

With increasing temperature, the probability of a removal of the faulty structure by rearrangement of the lattice particles (thermal aging) increases exponentially.

Imperfect crystals are not only formed by reactions in the solid state. There are many modes by which active states may be produced, for example, by (*a*) precipitation from solution, (*b*) rapid quenching of melts, (*c*) preparation at relatively low temperatures (decomposition), (*d*) electrochemical processes, (*e*) incorporation of

[5] Carl Wagner, "Theory of Tarnishing Processes, II," *Z. Phys. Chem.*, **B32,** 447 (1936).

[6] (*a*) Carl Wagner and W. Schottky, "Theory of Arranged Mixed Phases, I," *ibid.*, **B11,** 163 (1930).
(*b*) Carl Wagner, "Theory of Arranged Mixed Phases, II," *Z. Phys. Chem.* [Bodenstein-Festband], p. 177 (1931).
(*c*) Carl Wagner, "Theory of Arranged Mixed Phases: III, Disarranged Phenomena in Polar Compounds as Basis for Ionic and Electronic Conduction," *Z. Phys. Chem.*, **B22,** 181–94 (1933).
(*d*) W. Schottky, "Mechanism of Ionic Motion in Solid Electrolytes," *ibid.*, **B29,** 335 (1935).
(*e*) N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals. Oxford Univ. Press, London, 1940. 276 pp.

[7] E. Koch and Carl Wagner, "Formation of Ag_2HgI_4 from AgI and HgI_2 by Reaction in Solid State," *Z. Phys. Chem.*, **B34,** 317 (1936).

TABLE II

EFFECT OF PREPARATION ON LATTICE IMPERFECTION*

Mode of preparation			Avg. particle size (μ)		Avg. particle displacement (a.u.)	Fraction of amorphous material (%)	Molar heat of solution corrected for water content (K.-cal.)
Temp. (°C.)	Hr.	Water content (%)					
		Heated in vacuum	ZnO from $Zn(OH)_2$				
100	13	3.07	0.8		0.12	10–20	23.6
82	33	3.14	0.4–0.8		.11	10–20	23.0
300	5	0.66	0.8–1.2		.08	0	22.45
		Heated in N_2					
600	6	0.03	0.8–1.6		0	0	22.3
			α-Fe_2O_3 from α-FeOOH Hexagonal axes (a.u.)				
		Heated in vacuum	(a)	(c)			
240	1	1.68	181	100	.21	0	54.0
		Heated in air					
300	1	1.45	191	103	.18	0	51.5
410	1	0.89	191	151	.11	0	50.7
600	1	0.36	204	180	0	0	49.3

* From R. Fricke and co-authors (see footnote 9).

small amounts of impurities, and (*f*) mechanical treatment.

Any deviation of a crystal from its equilibrium state may be designated as a topochemically disordered state.

An example of an expanded lattice[8] is given in Table I. Tricalcium silicate when freshly prepared by reaction in the solid state, $CaCO_3 + Ca_2SiO_4 \rightarrow Ca_3SiO_5 + CO_2$, possesses an anomalously expanded lattice, which is shown by the fact that all angles of reflection of powder photographs are somewhat smaller than in the normal compound. Tricalcium silicate is the most valuable component of Portland cement. The stretching of the lattice is one of the conditions for good binding properties of the cement. Although tricalcium silicate is not stable at ordinary temperature, its lattice can be preserved by rapid cooling. The quenching before aging improves the quality of the cement because the expanded lattice is frozen in.

Uniformly expanded lattices are comparatively rare; irregular distortions without change of the lattice parameters are more frequent. Table II shows as an example the distorted state in which zinc oxide and α-iron oxide[9] may be prepared by a careful dehydration of the respective hydroxides. The average distortion is greater the lower the temperature of the preparation. The correlation between the different properties measured is evident. The more the particles are displaced from their normal positions and the smaller the particle size, the greater is the excess energy content (measured by the molar heats of solution). At higher temperatures, the thermal mobility causes the lattice particles to approach their normal positions. The crystals are growing and the content of amorphous material, the lattice distortion, and the content of excess energy are reduced. In the case of α-iron oxide, the excess energy amounts to more than 10% of the normal energy content. Such a difference in activity can have a tremendous influence on the rate of solid-state reactions.

A versatile way of obtaining solids in various topochemical states is the precipitation from solution. The solids are aged in contact with a suitable liquid until the desired state is reached, at which time the aging is interrupted by removal of the liquid.[10]

Because it is always possible to vary (within limits) arbitrarily the state of solids which are brought to react with each other, it is also possible to influence to a certain extent the course of a reaction and the properties of the reaction products. Figure 2 shows that any circumstance by which the activities of reacting phases are increased also increases the gradient of the chemical potential of the diffusing particles in the layer of the reaction products and consequently the reaction rate. All lattice imperfections obviously cause an increase in activity. This fact is brought out by the following examples.

The reaction of lime with iron oxide becomes faster when the iron oxide has a topochemically faulty structure, even when the grain size is larger than that of a relatively perfect oxide.[11] Figure 4 shows the difference in reactivity between a topochemically faulty oxide (prepared by decomposition of iron sulfate) and a comparatively perfect oxide (prepared by decomposition of iron oxalate). Despite greater grain size, the "sulfate oxide" reacts much faster with lime. At higher temperatures, the differences in activity are eliminated.

[8] W. Jander, "Reactions in Solid State at High Temperatures: XVIII, Tricalcium Silicate, Most Important Constituent of Portland Cement Clinker," *Angew. Chem.*, **51,** 696–99 (1938); *Ceram. Abs.*, **18** [8] 203 (1939).

[9] (*a*) R. Fricke and E. Gwinner, "Quantitative Interpretation of Irregular Lattice Distortions and Impurities of Amorphous Material in Active Substances," *Z. Phys. Chem.*, **A183,** 165 (1938).

(*b*) R. Fricke and P. Ackermann, "Thermal and X-Ray Characterization of Irregular Lattice Distortions in Zinc Oxide," *Z. Anorg. Allgem. Chem.*, **214,** 177 (1933).

(*c*) R. Fricke and P. Ackermann, "Heat Content and Lattice Structure of Active Ferric Oxide," *Z. Elektrochem.*, **40,** 630 (1934).

[10] I. M. Kolthoff and C. W. Carr, "Studies on Aging and Coprecipitation: XXXVII, Distribution Coefficient of Arsenate Between Magnesium Ammonium Phosphate and Solution," *Jour. Phys. Chem.*, **47,** 148–52 (1943); *Chem. Abs.*, **37,** 3321[4] (1943); see also previous publications on aging and coprecipitation.

[11] J. A. Hedvall and S. O. Sandberg, "Reactions in Solid State of Mixtures of Active Fe_2O_3 and CaO," *Z. Anorg. Allgem. Chem.*, **240** [1] 15–20 (1938); *Ceram. Abs.*, **19** [1] 32 (1940).

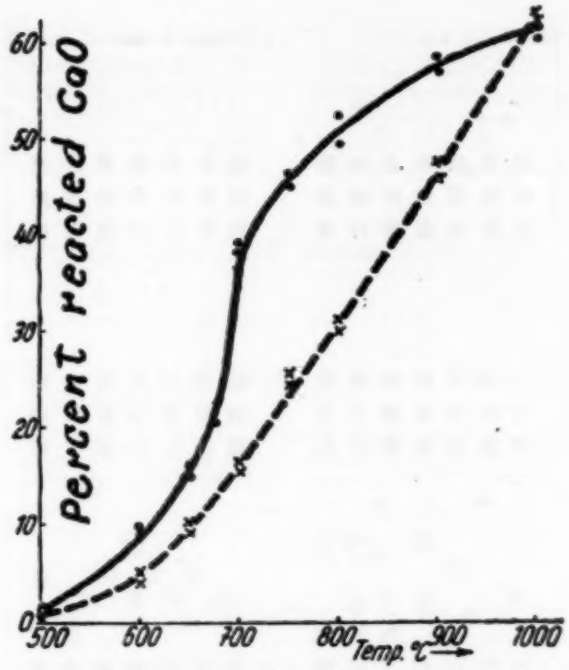

FIG. 4.—Different reactivities of iron oxide (from Hedvall and Sandberg[11]); *solid line*, "sulfate oxide" + lime; *broken line*, "oxalate oxide" + lime.

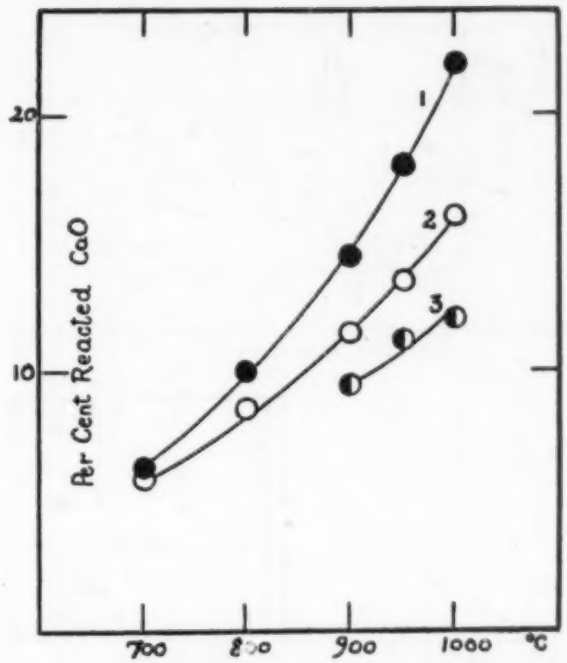

FIG. 5.—Effect of preheating quartz on reactivity (from Hedvall, *et al.*[12]); curve (1), preheated in O_2 or in SO_3; curve (2), preheated in air; curve (3) preheated in SO_3.

An instance of topochemical particularities produced by a pretreatment of one of the reacting components is found in the formation of calcium silicate from lime and silica[12] (Fig. 5). The silica had been preheated in the presence of gases which cannot interact chemically with silica in the usual sense (oxygen, sulfur dioxide, and sulfur trioxide) but which do nevertheless affect the lattice state by penetration or dissolution. Quartz, which had been heated in sulfur trioxide, was the least active. Heating in air increased the activity, and greater increase was found by heating in oxygen or in sulfur dioxide.

A reacting component has a greater reactivity when it is formed directly in contact with its partner. The formation of magnesium chromite from magnesia and ferrous chromite thus becomes strengthened when the magnesium oxide is replaced by magnesium carbonate which decomposes at the temperature of the reaction[13] (Fig. 6).

An especially active state occurs during the course of a crystallographic transformation because the bonds between the particles are weakened or even broken in the transition. During the process of the transition,

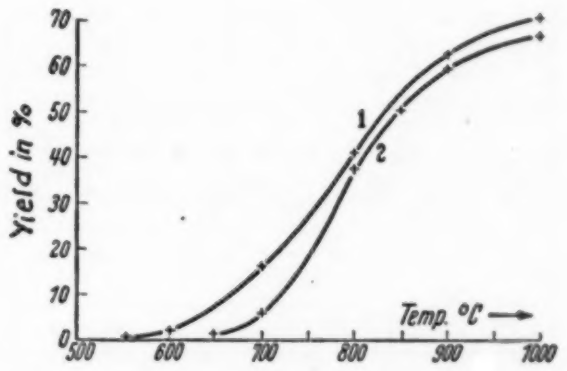

FIG. 6.—Effect of thermal decomposition on reactivity (from Hedvall and Ny[13]); curve (1), $MgCO_3 + Cr_2FeO_4 \rightarrow Cr_2MgO_4 + FeO + CO_2$; curve (2), $MgO + Cr_2FeO_4 \rightarrow Cr_2MgO_4 + FeO$.

the crystal invariably has a maximum activity in reactions with surrounding phases (Hedvall's rule). Figure 7 shows the relative rate maximum of the reaction, $BaO + 2AgI \rightarrow BaI_2 + Ag_2O$,[14] at the transition point of silver iodide (145°C.). The maximum of the reactivity can of course be found only when the time of reaction is of the same order of magnitude as the time within which the transition occurs.

[12] J. A. Hedvall, S. Alfredsson, K. Ohlsson, O. Runehagen, S. Waldenström, and S. Åkerström, "Reactivity and Effects of Lattice Distortion in Important Glass-Technical and Ceramic Systems," *Glastech. Ber.*, **20**, 34 (1942).

[13] J. A. Hedvall and V. Ny, "Double Decomposition in Solid State Between Synthetic or Mineral Ferrochromite and Magnesium Oxide or Magnesium Carbonate," *Z. Anorg. Allgem. Chem.*, **235** [1–2] 148–52 (1937); *Ceram. Abs.*, **19** [4] 101 (1940).

[14] J. A. Hedvall, E. Garping, N. Lindekrantz, and L. Nelson, "Role of Ions and Crystallographic Transformation in Reactions in Solid State," *Z. Anorg. Allgem. Chem.*, **197**, 399–421 (1931); *Ceram. Abs.*, **11** [8] 470 (1932).

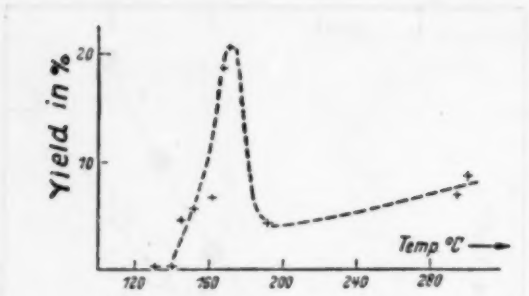

FIG. 7.—Relative rate maximum at crystallographic transition point (from Hedvall, *et al.*[14]).

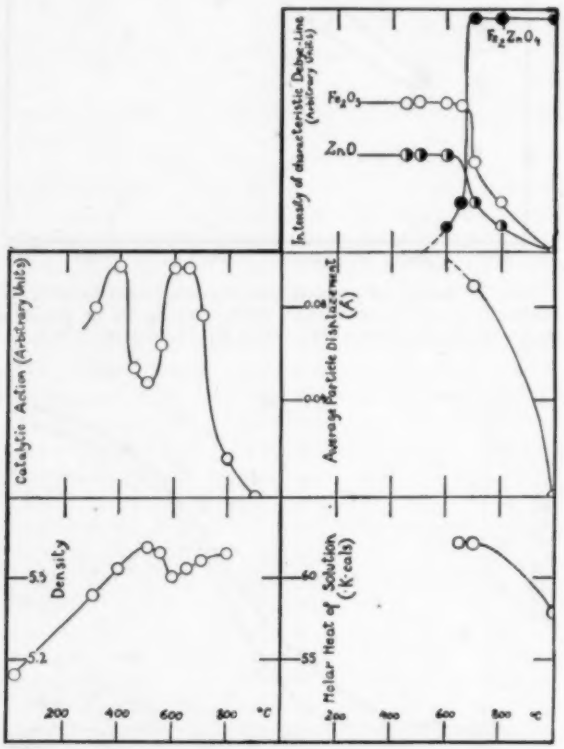

FIG. 8.—Intermediate stages of zinc-iron-spinel formation.

V. Qualitative Picture of Course of Simple Additive Reaction

Because extra-thermodynamic variations of the properties of reacting solids occur in most cases, it is usually possible to understand the reactions only qualitatively. Intensive research has been carried out on the spinel formation as a relatively simple and representative example of an additive reaction (A + B → AB).

The formation of zinc iron spinel from zinc oxide and iron oxide, for example, is described. The mechanism has been deduced indirectly from various independent measurements. The powder mixtures of zinc oxide and iron oxide were kept for given times at given temperatures, and the changes of certain physical or chemical properties were determined. Some of these measurements are shown in Fig. 8 in which are plotted the densities of the reacting system,[15] the catalytic action on the reaction,[16] $CO + O_3 \rightarrow CO_2$ at 250°C., the intensity of one characteristic Debye line of each component,[17] and the average particle displacement in the spinel lattice and the molar heat of solution.[18] At each temperature of observation, a certain period of the reaction has occurred. The intermediate stages are shown schematically in Fig. 9. The temperatures, however, at which the reaction proceeds to a certain extent within a given time are not characteristic. The same sequence of steps, for instance, would have taken place at lower temperatures in longer periods of time.

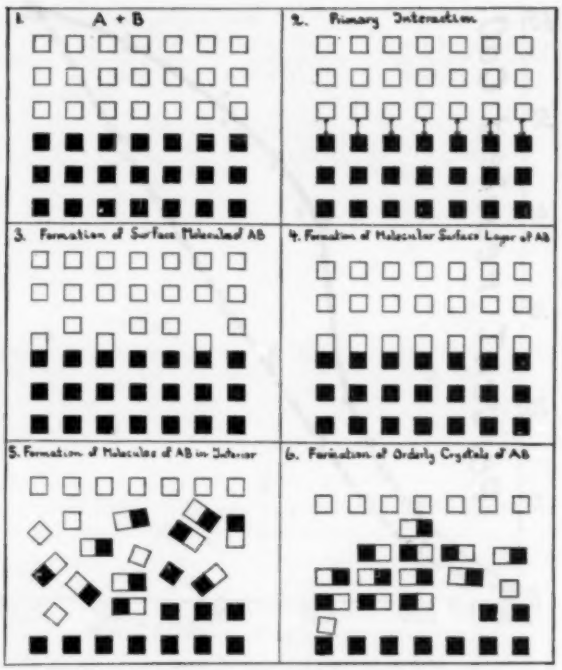
1. A + B
2. Primary Interaction
3. Formation of Surface Molecules of AB
4. Formation of Molecular Surface Layer of AB
5. Formation of Molecules of AB in Interior
6. Formation of Orderly Crystals of AB

FIG. 9.—Schematic mechanism of spinel formation.

(1) Period of Primary Interaction

Already upon mixing the reacting components (abbreviated to A and B) at ordinary temperature, an interaction is observed unless the substances are thoroughly aged. This interaction may increase appreciably the number of adsorbing centers at the surface.

[15] G. F. Hüttig, H. E. Tschakert, and H. Kittel, "Investigation on Course of Zinc Ferrite Formation from Zinc Oxide and Iron Oxide," *Z. Anorg. Allgem. Chem.*, **223**, 241 (1935).

[16] G. F. Hüttig, D. Zinker, and H. Kittel, "Active Stages Encountered During Transformation of Mixture of Metal Oxides into Chemical Combination," *Z. Elektrochem.*, **40**, 306 (1934).

[17] W. Jander and H. Hermann, "Reactions in Solid Substances at High Temperatures: XXIII, Theory of Active Structures Appearing at Beginning of Reactions in Solid State," *Z. Anorg. Allgem. Chem.*, **241**, 225–32 (1939).

[18] R. Fricke and W. Dürr, "Active Substances: XXXVII, Thermochemical and X-Ray Investigation of Reactions During Formation of Zinc-Iron Spinel from Active Zinc Oxide and Various Kinds of Ferric Oxide," *Z. Elektrochem.*, **45**, 254 (1939).

Figure 10 shows that the adsorption of lead nitrate by zinc oxide and iron oxide is increased about six fold upon mixing the oxides.[19] This increase of the adsorption apparently is connected with the circumstance that zinc oxide and iron oxide can combine chemically; it is not observed, for instance, in mixtures of iron oxide and chromic oxide.

Slight heating of the reaction mixture, however, causes the surfaces of the particles to become more closely attached to each other so that the specific surface as determined by the amount of organic dyes adsorbed decreases and the density increases.

(2) Formation of Surface Molecules (Period of First Activation)

At relatively low temperature, some surface particles of A or of B become mobile enough to swing out from their original positions and to become attached to the surface of the other component. A surface molecule of AB is thus formed without a diffusion into the other lattice and without formation of the correct AB structure. The surface molecules, moreover, do not form a coherent film and they are loosely bound. In this stage, the reaction mixture shows a low density and a maximum catalytic action. There is apparently not only a maximum of the reaction yield but also a maximum of the apparent activation energy, and therefore a real maximum of the catalytic efficiency. The latter has been found in the formation of zinc aluminum spinel from zinc oxide and aluminum oxide.[20]

(3) Formation of Molecular Surface Film (Period of First Deactivation)

At more elevated temperatures (or in longer periods of time), a complete layer of AB molecules is formed by surface diffusion of the mobile component. The film is relatively stable and the molecular forces between the AB molecules are balanced. The catalytic activity is, therefore, markedly lower, with a further increase in the density of the reaction mixture.

The processes described occur only at the surfaces or phase boundaries by a motion of surface particles which have enough surplus energy. These stages are therefore very dependent on the state of the reacting components. The interaction between A and B would not be disclosed by chemical analysis or by X-ray measurements.

(4) Formation of Molecules of AB by Diffusion in Interior (Period of Second Activation)

By further increase of the temperature, the thermal activation is sufficient to enable the diffusing particles to penetrate into the interior of the other lattice through the first layer of the reaction product. An unstoichiometrically composed layer of AB in A or B is

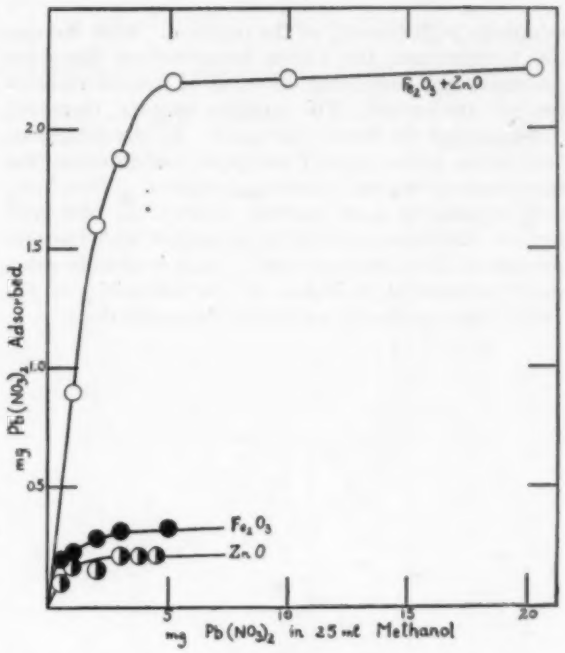

FIG. 10.—Increased adsorption by reaction mixture (from Starke[19]).

formed. By reaction at the phase boundary, fresh layers of AB are produced. The reaction product in the beginning is in a very imperfect and disordered state. The catalytic activity of this state again represents a maximum, whereas the loose form of the reaction product causes a minimum of the density. It is remarkable that in the case of the zinc iron spinel formation the reaction product soon possesses the correct though very imperfect crystal structure. The first practically amorphous layers can be only a few molecules thick. This is evident from the fact that the Debye lines of the spinel appear as soon as the intensities of the lines of the zinc oxide and iron oxide begin to decrease. In this stage, however, some extra lines also appear, indicating a possible deviation from the normal spinel structure.[17] The lines of the spinel are quite sharp from the beginning,[18] showing that the number of nuclei of the new phase must be small. In the beginning, the size of the spinel crystals must be very small so that the X-ray diffraction lines should have considerable breadth; since this is not observed, the number of crystals must be small and are first detected after a certain growth. In other cases, however, appreciable amounts of amorphous reaction product may be formed in this period if the crystallization is hindered.

(5) Formation of Orderly Crystallized Reaction Product (Period of Second Deactivation)

The freshly formed reaction product has an imperfect lattice, and this is evident from the average lattice distortion and the anomalously large heat of solution. The distorted state makes possible a relatively rapid diffusion through the layer of reaction product, that is, a

[19] K. Starke, "Surface of Catalytic Mixtures and Surface Changes Caused by Reaction in Solid State," *Z. Phys. Chem.*, **B37**, 81 (1937).

[20] W. Jander and K. Bunde, "Reactions in Solid State at High Temperatures: XIV, Intermediate Steps in Formation of Zinc Aluminate from Zinc Oxide and Aluminum Oxide in Solid State," *Z. Anorg. Allgem. Chem.*, **231**, 345–64 (1937); *Ceram. Abs.*, **18** [1] 37 (1939).

relatively high velocity of the reaction. With increasing temperature, the lattice imperfections disappear gradually and increasing amounts of normal reaction product are formed. The catalytic activity, therefore, decreases and the density increases. By the disappearance of the active state of the spinel, the diffusion (the reaction rate) becomes increasingly slower. When, however, a perfectly aged reaction product, has first been formed, the kinetics could be described with thermodynamics. The reaction at this stage is already practically completed as shown by the intensities of the Debye lines or also by analytical determinations.

VI. Conclusions

Only a small fraction of the great variety of reactions in the solid state has been discussed. In practice, the conditions which determine and influence the reaction rate are usually considerably more complicated, especially when more than one solid phase can be formed from the same reacting components. In recent years, however, the factors involved have been recognized so that it appears always possible to obtain a qualitative insight in a reaction although quantitative relations are hardly to be expected in the near future.

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